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Vol. 27, No. 5 November 1941

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MATHEMATICAL TABLES

A list of the mathematical tables now obtainable from the National Bureau of Standards is printed on page 3 of the Journal cover. New tables will be announced from time to time as they become available.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1429

Part of Journal of Research of the National Bureau of Standards, Volume 27, November 1941

SUGAR ACETATES, ACETYLGLYCOSYL HALIDES, AND ORTHOACETATES IN RELATION TO THE WALDEN INVERSION[1,2]

By Harriet L. Frush and Horace S. Isbell

ABSTRACT

The tendency of the acetyl groups in the sugar acetates and glycosyl halides to form intramolecular condensation products depends upon the stereomeric arrangement of the groups within the molecule. In this paper the stereomeric factors which control the formation of orthoesters are discussed in light of the opposite-face concept for the Walden inversion, and it is shown that cyclic orthoacetates are formed when an acetyl group can approach the face of a neighboring carbon opposite a replaceable halogen atom. This concept was tested by application of the Koenigs-Knorr reaction to pentaacetyl-α-*d*-α-guloheptopyranosyl bromide and to heptaacetyl-α-neolactosyl chloride. Both of these compounds gave, as anticipated, the corresponding methyl orthoacetates.

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I. INTRODUCTION

The sugar acetates and their derivatives are among the most important sugar compounds from the standpoint of their general usefulness for analytical purposes, in synthesis, and in the elucidation of structure. Methods for the preparation of the fully acetylated derivatives were discovered early in the history of sugar chemistry, and several of the sugar acetates were obtained in crystalline form. In some cases two crystalline acetates were prepared from the same sugar,

[1] The material in this paper was abstracted from a thesis submitted by Harriet L. Frush, of this Bureau, in May 1941 to the Faculty of the Graduate School of the University of Maryland, represented by Nathan L. Drake, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] This paper was presented before the division of Sugar Chemistry and Technology of the American Chemical Society at Atlantic City, N. J., September 1941.

and it became apparent that these were alpha and beta modifications analogous to the methyl glycosides. Today a large number of the crystalline sugar acetates are known in both alpha and beta modifications, and are widely used in the characterization of the sugars and their derivatives. Because the acetyl linkage can be removed readily, and yet is comparatively stable, acetylation has frequently been employed to protect part of the hydroxyls in the sugar molecule in the course of reactions involving the remaining groups. Thus the acetylated sugars have proved to be valuable starting materials in the synthesis of other derivatives.

Even more useful than the sugar acetates in synthetic processes are their halogen derivatives, the acetylglycosyl halides, prepared by reaction of the hydrogen halide upon the acetate, and having the halogen attached to the glycosidic carbon. Since this halogen is particularly reactive in comparison with the acetyl groups, the acetylglycosyl halides may be used in a wide variety of reactions involving replacement on the glycosidic carbon. Thus an acetylglycosyl halide may be condensed with alcoholic hydroxyl groups in the presence of a basic condensing agent (for example, silver oxide or carbonate, or quinoline) to form glycosides, substances which are widely distributed in plant and animal life. Consequently, the acetylglycosyl halides of the sugars have an essential part in the synthesis of compounds which are important in biochemical research and have practical applications in the fields of pharmacology and medicine. Numerous syntheses of natural glycosides have already been carried out, frequently through the reaction of the nonsaccharide constituent with an acetylglycosyl halide.

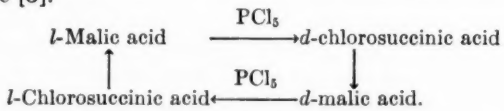
A special group of glycosides, the disaccharides, may be prepared by condensation of acetylglycosyl halides with certain sugar derivatives. By treating tetraacetyl-α-*d*-glucosyl bromide with tetraacetyl-*d*-glucose in the presence of silver carbonate, Fischer synthesized isotrehalose (β,β-trehalose) [1],[3] and by similar methods other workers, especially Helferich, Freudenberg, and Evans, have prepared many compound sugars. In these condensations the alpha acetylglycosyl halide is usually combined with a sugar having one free hydroxyl group, and the resulting disaccharide is formed with a Walden inversion on carbon 1, so that these syntheses generally lead to disaccharides with a beta type of union. One might anticipate that the alpha type of union could be obtained by the use of the beta acetylglycosyl halide, but the preparations have not generally been successful. A few beta acetylglycosyl chlorides have been obtained by treatment of the corresponding alpha acetylglycosyl bromide with an especially prepared silver chloride [2], but many of these beta compounds are unstable and in condensation reactions give complex mixtures from which crystalline products are not readily separable.

Since replacement occurs with inversion at carbon 1, the difference in behavior of the alpha and beta acetylglycosyl halides is, no doubt, related to the mechanism of the Walden inversion. A brief review of the Walden inversion, especially in relation to the opposite-face mechanism, will afford a basis for the discussion of the replacement reactions of the acetylglycosyl halides.

[3] Figures in brackets indicate the literature references at the end of this paper.

II. WALDEN INVERSION

In 1896 Walden reported an inversion of optical rotation in the conversion of malic to chlorosuccinic acid by reaction with phosphorus pentachloride [3].



Since this brief report the phenomenon, which has come to be known as the Walden inversion, has been extensively studied with numerous reactants and optically active substances [4, 5]. Perhaps the most satisfactory explanation for the change in configuration was suggested by Werner in 1911 [6] and is commonly known as the opposite-face mechanism for the Walden inversion. Werner pointed out that in the tetrahedron formed by the groups *A*, *B*, *D*, and *X* attached to a carbon, there are four positions at which an entering group may become attached, with the displacement of group *X*, namely the four faces *ABX*, *BDX*, *DAX*, or *ABD*. It will be observed in figure 1 that substitution for *X* at one of the first three of these faces will cause no change in configuration, but when the entering group, *Y*, approaches the face opposite *X* (*ABD*), with simultaneous withdrawal of *X*, a shift to the enantiomorphic configuration must occur. Garner [7] clarified the Werner concept by means of an ingenious mechanical model showing this shift in valences, which is comparable to the turning inside out of an umbrella.[4]

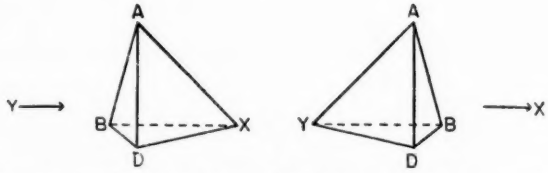


FIGURE 1.—*Opposite-face mechanism for the Walden inversion.*

The sugars and their derivatives are uniquely adapted to the study of the inversion mechanism, since, with the carbon atoms bound in a ring, rotation about the carbon-carbon bonds is largely restricted, and the spheres of influence of the various groups within the molecule are oriented in relation to one another. Recently, Isbell [9] pointed out that in certain replacement reactions intramolecular condensations take place when reactive groups within the sugar molecule can approach the face of the carbon opposite its replaceable group (halide, tosyl, etc.) and that the opposite-face concept appears to provide a satisfactory explanation for the formation or lack of formation of intramolecular condensation products, among which are the anhydrosugars and the orthoesters. Inasmuch as some of these intramolecular condensation products are formed when the acetylglycosyl halides are used for the preparation of glycosides, it seemed desirable to investigate more fully the replacement reactions of the acetylglycosyl halides in relation to the opposite-face concept.

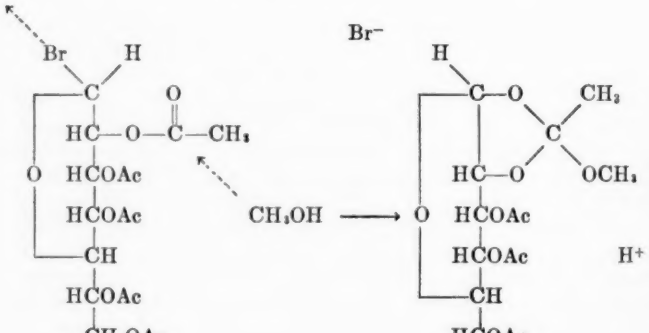
[4] A comprehensive discussion of the Walden inversion and the work which has led to the acceptance of the opposite-face mechanism may be found in chapters V and VI of reference [8].

III. REPLACEMENT REACTIONS OF THE ACETYLGLYCOSYL HALIDES

The replacements studied in this investigation have involved the reaction between certain acetylglycosyl halides and methyl alcohol in the presence of silver carbonate, a reaction used almost simultaneously by Koenigs and Knorr [10] and by Fischer and Armstrong [11], and commonly referred to as the Koenigs-Knorr reaction. In some cases, the first of which was reported by Fischer, Bergmann, and Rabe [12], this reaction leads to the formation of substances which do not have the properties of normal glycosides. As shown simultaneously by Freudenberg and Braun [13], and by Haworth and coworkers [14, 15], one of the acetyl groups is joined to the glycosidic carbon and to the adjacent carbon in a cyclic orthoacetic ester structure. According to Isbell [9], the orthoacetate seems to be formed by an intramolecular reaction in which an acetyl group approaches the face of carbon 1 opposite the departing halogen, and combines with inversion. Presumably, as the bromine is removed by combination with the silver carbonate or other suitable reagent, the carbonyl oxygen is attracted to the opposite face of carbon 1, leaving the acetyl carbon deficient in electrons. The deficiency is satisfied by the attraction of a negative group, in this case methoxyl, from the environment. Electronically the reaction may be considered to consist in a flow of electrons from the hydrogen of the methyl alcohol to the methoxyl, from the methoxyl to the acetyl carbon, to the oxygen, to the glycosidic carbon, and to the bromine. This results in the formation of a hydrogen ion, a bromide ion, and the methyl orthoacetate. The process is represented by the following equations. The reactions are driven to the right by removal of either the bromide ion or the hydrogen ion, the former by use of silver oxide or carbonate, the latter by use of pyridine or quinoline.

REACTIONS WHEN ACETYL GROUP CAN APPROACH FACE OF CARBON 1 OPPOSITE THE HALOGEN ATOM

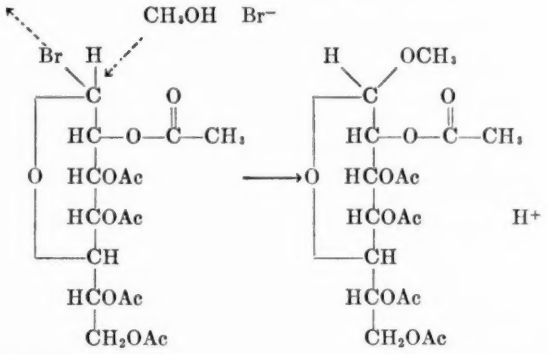
Orthoester reaction



Pentaacetyl-α-*d*-α-gulo-heptosyl bromide

Tetraacetyl-*d*-α-gulohep-tose methyl orthoacetate

Competitive glycosidic reaction

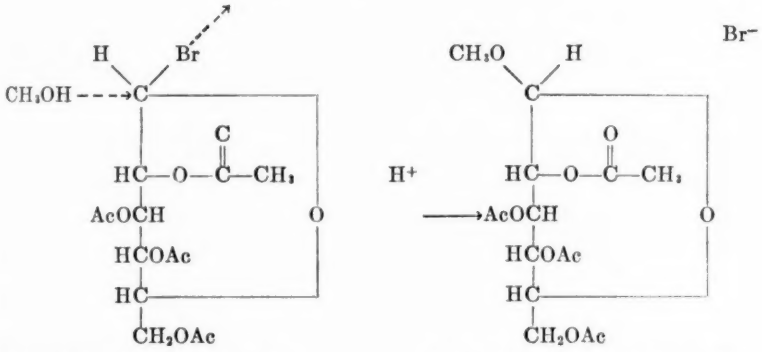


Pentaacetyl-α-*d*-α-guloheptosyl bromide

Methyl pentaacetyl-β-*d*-α-guloheptoside

REACTION WHEN ACETYL GROUP CANNOT APPROACH FACE OF CARBON 1 OPPOSITE THE HALOGEN ATOM

Glycosidic reaction



Tetraacetyl-α-*d*-glucosyl bromide

Methyl tetraacetyl-β-*d*-glucoside

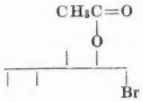
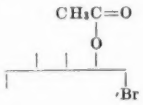
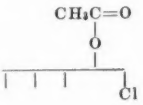
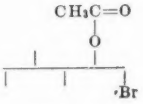
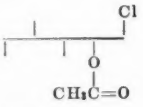
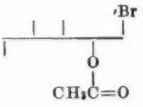
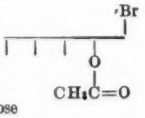
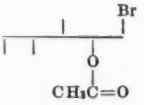
The orthoacetate is formed only when the carbonyl oxygen of an acetyl group can approach the face of the carbon opposite the halogen. This is possible when the acetyl group and halogen atom lie on opposite sides of the plane of the sugar ring. As shown in the equations, when the halogen and the acetyl group of carbon 2 of an aldose are on the same side of the ring, the carbonyl oxygen of the acetyl group is unable to approach carbon 1 at the face opposite the departing halogen, and therefore it cannot form the orthoacetate. Under these circumstances the halogen is replaced with inversion by a negative group from the environment, methoxyl in this case. This is the ordinary Koenigs-Knorr reaction, which leads to the formation of normal glycosides. However, when the halogen and the adjacent acetyl group are on opposite sides of the ring, either the acetyl group of the adjacent carbon or the methoxyl group from the environment is capable of approaching the face of carbon 1 opposite the departing halogen, and

combining with inversion. One of these reactions gives the normal glycoside, the other the orthoester, and the two reactions may be conceived as occurring in competition, so that ordinarily both products are formed. The separation of crystalline isomers from the mixture is frequently difficult, and consequently the lack of a crystalline derivative is not satisfactory evidence of failure to form the orthoester.

Crystalline methyl orthoacetates have been prepared for rhamnose, lyxose, mannose, 4-glucosido-mannose, ribose, talose, α-glucoheptose, fructose, sorbose, turanose, and maltose. The structure and configuration of the parent acetylglycosyl halides are known with reasonable certainty for all of these compounds with the exception of maltose. Since the methyl orthoacetate of maltose was prepared from an "acetochloromaltose," which supposedly has a chloro-orthoester structure [16], the formation of the methyl orthoacetate of maltose presumably involves the replacement of the chlorine in a structure already existing, and not the reaction being considered here. Inasmuch as carbon 1 of the ketoses is free to rotate about the carbon-carbon axis, the acetyl group of carbon 1 can always be brought into a favorable position for the orthoester reaction, and all ketoses are therefore capable of orthoester formation. Aside from the derivatives of maltose and the ketoses, the methyl orthoacetates so far prepared have been formed from acetylglycosyl halides in which the acetyl groups of both carbons 2 and 3 are *trans* to the halogen. Although the configuration of carbon 3 may to some extent influence orthoester formation, it is believed that it plays only a limited part, according to the mechanism outlined, and that the essential configuration is a *trans* relationship between the halogen atom and a neighboring >C=O group.

As may be observed from the compilation of data shown in table 1, only acetylaldosyl halides having the α-mannose, α-talose, and β-gulose configurations have heretofore been reported to give methyl orthoacetates. According to the opposite-face hypothesis, acetylaldosyl halides having the α-altrose, α-idose, β-galactose, β-allose, and β-glucose configurations should also give orthoesters.

TABLE 1—*Aldose sugars which have yielded methyl orthoacetates*

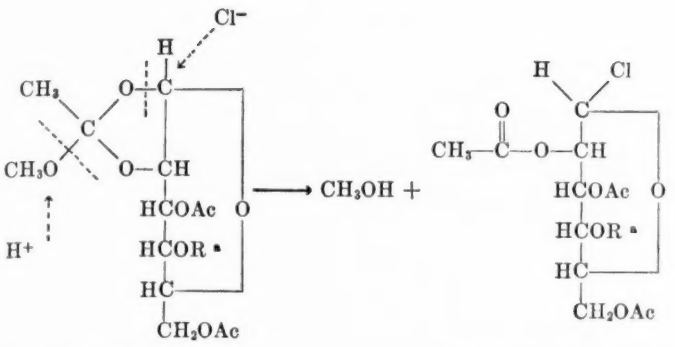
Ring configuration	Sugars	Orthoacetate prepared
A. FROM THE ALPHA ACETYLGLYCOSYL HALIDE		
Mannose 	Rhamnose	Fischer, Bergmann, and Rabe, 1920 [12].
	Lyxose	Levene and Wolfrom, 1928 [17].
	Mannose	Dale, 1924 [18].
	4-Glucosido-mannose	Isbell, 1931 [19].
Talose 	Ribose	Levene and Tipson, 1931 [20].
	Talose	Pigman and Isbell, 1937 [21].
	α-Guloheptose	This investigation.
Altrose 	Neolactose	This investigation.
Idose 	Not investigated	
B. FROM THE BETA ACETYLGLYCOSYL HALIDE		
Gulose 	α-Glucoheptose	Haworth, Hirst, and Stacey, 1931 [2].
Galactose 	Not investigated	
Allose 	Not investigated	
Glucose 	Not investigated	

In the foregoing discussion the configurations of the alpha and beta acetylglycosyl halides have been tacitly assumed, but unfortunately these configurations have not been rigorously established. Apparently the optical rotations of the alpha and beta acetylglycosyl halides parallel the optical rotations of the alpha and beta acetates, glycosides, and sugars, and presumably *the more dextrorotatory member of the alpha-beta pair in each series has the d-configuration for carbon 1.* The configurations ordinarily assigned for the alpha and beta acetylglycosyl halides, and used here, are based on this premise. Although there is no direct proof for the correctness of the premise, the chemical properties of the alpha and beta isomers support the structures assigned.[5] However, it is recognized that the validity of our generalizations is dependent upon the correctness of these assignments.

To test the opposite-face hypothesis for orthoester formation, we undertook the preparation of an orthoacetate from an acetylaldosyl halide having the α-altrose configuration. The compound used was was heptaacetyl-α-neolactosyl chloride (heptaacetyl-4-β-*d*-galactosyl-α-*d*-altrosyl chloride), first reported by Kunz and Hudson [23]. The material required for the investigation was prepared by the excellent method of Richtmyer and Hudson [24]. In harmony with the opposite-face hypothesis, heptaacetyl-α-neolactosyl chloride on treatment with methyl alcohol, in the presence of silver carbonate and Drierite (anhydrous calcium sulfate), gave a 70-percent yield of hexaacetylneolactose methyl orthoacetate, and in addition about 30 percent of methyl heptaacetyl-β-neolactoside. The formation of both hexaacetylneolactose methyl orthoacetate and methyl heptaacetyl β-neolactoside is in accord with the existence of anintramolecular reaction and a competing extramolecular replacement with inversion, essentially as represented in the equations on pages 416 and 417. The compound obtained in 70-percent yield shows the reactions and properties which characterize the sugar methyl orthoacetates, including stability of the orthoacetate group toward alkaline hydrolysis [12, 18] and formation of the acetyl-glycosyl halide by reaction with hydrogen chloride in anhydrous chloroform solution [19].

When the latter reaction was first observed by one of the authors for the methyl orthoacetate of 4-glucosido-mannose, an interpretation was suggested which involved the formation of an intermediate addition compound with hydrogen chloride. A more simple interpretation can now be made in light of our present knowledge of the mechanism of replacement reactions involving inversion. Thus the reaction of the orthoester with hydrogen chloride or similar reagent can be considered as the reverse of the reaction leading to orthoester formation. Presumably the negative halide ion approaches the face of the glycosidic carbon opposite the orthoester linkage and combines, while simultaneously the orthoester linkage is broken. Electronically the reaction represented below may be considered as a flow of electrons from the chloride ion to the glycosidic carbon, to the oxygen, to the acetyl carbon, and to the methoxyl group, which then combines with a proton. This results in the formation of the acetylglycosyl halide and methyl alcohol.

[5] Micheel and Micheel [22] have postulated configurations based on optical rotations, and have found that the acetylglycosyl halides having a *cis* relationship for the halogen atom of carbon 1, and the acetyl group of carbon 2, yield quaternary ammonium salts when treated with the tertiary bases, but that acetylglycosyl halides having a *trans* relationship fail to react.



Hexaacetylneolactose methyl 1,2-orthoacetate

Heptaacetyl-α-neolactosyl chloride

* R is the tetraacetyl-β-*d*-galactosyl group.

To obtain further information as to the general applicability of the opposite-face hypothesis in relation to orthoester formation, we undertook the preparation and study of a number of acetylglycosyl halides in the heptose series. This work, which is still in progress, has led to the preparation of an orthoester of *d*-α-guloheptose.

The formation of the orthoester of *d*-α-guloheptose required the successive preparation of hexaacetyl-α-*d*-α-guloheptose and pentaacetyl-α-*d*-α-guloheptosyl bromide, and the application of the Koenigs-Knorr reaction to the latter substance. Hexaacetyl-α-*d*-α-guloheptose was obtained by low-temperature acetylation, with acetic anhydride and pyridine, of crystalline α-*d*-α-guloheptose. The manner of preparation of the new acetate supports its classification as the modification analogous to that of the sugar; that is, as hexaacetyl-α-*d*-α-guloheptose. Pentaacetyl-α-*d*-α-guloheptosyl bromide was obtained by treating hexaacetyl-α-*d*-α-guloheptose with hydrogen bromide at 0°C. The product crystallizes readily and, when pure, is relatively stable. The reaction of the new bromide with methyl alcohol in the presence of silver carbonate and Drierite was studied by analysis of the solution after reaction was complete, and by isolation and analysis of the reaction product.

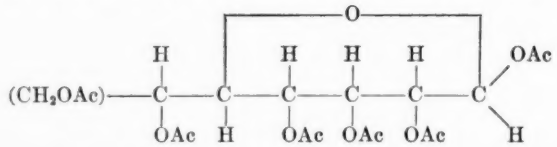
The orthoacetyl group is readily hydrolyzed by acid but is stable to alkali, whereas the ordinary acetyl group is hydrolyzed by either reagent. Consequently the analysis of the solution obtained from the Koenigs-Knorr reaction was made by acetyl determinations in acid and in alkaline solution. Upon the basis of the difference in the results of the acid and alkaline hydrolyses, the conversion of pentaacetyl-α-*d*-α-guloheptosyl bromide to the acetylated orthoester was calculated to be nearly quantitative.

Upon evaporation of the solution, a crystalline product was obtained in nearly quantitative yield, and the product gives the reactions characteristic of the orthoester derivatives. As already noted, one acetyl group (the orthoacetyl) is resistant to alkaline hydrolysis

but is easily hydrolyzed by acid. The compound reacts rapidly with an anhydrous solution of hydrogen chloride in chloroform to give a strongly levorotatory substance. The crystalline residue, which appears to be pentaacetyl-α-*d*-α-guloheptosyl chloride, is being investigated further.

IV. EXPERIMENTAL DETAILS

1. HEXAACETYL-α-*d*-α-GULOHEPTOPYRANOSE



Five grams of finely powdered α-*d*-α-guloheptose [6] was acetylated by the use of 28 ml of acetic anhydride and 35 ml of pyridine. The acetylation mixture was stirred in an ice bath for 2 days, then poured, with stirring, into ice water. After a short time the acetate separated as a gum, the water was decanted, and a fresh quantity of ice water was added, from which in the course of about an hour, with continuous stirring, a crystalline substance separated. The acetate, largely hexaacetyl-α-*d*-α-guloheptopyranose, weighed 7.5 g and melted at 115° C, approximately. A total of 13.2 g of crystalline material, obtained from two acetylations, was recrystallized several times from ethyl alcohol, in which the compound is quite soluble. Hexaacetyl-α-*d*-α-guloheptopyranose crystallizes from ethyl alcohol in chunky rectangular prisms (fig. 2, *A*) which melt at 126° C and give $[\alpha]_D^{20} = -62.8°$. *Analysis:* Calculated for $C_{19}H_{26}O_{13}$: C, 49.35; H, 5.67. Found: C, 49.47; H, 5.64.

2. PENTAACETYL-α-*d*-α-GULOHEPTOPYRANOSYL BROMIDE

The new hexaacetyl-α-*d*-α-guloheptopyranose (6.8 g) was treated at 0° C with 35 ml of a saturated solution of hydrogen bromide in acetic acid and with 3.5 ml of acetic anhydride. After the acetate had dissolved, the solution was kept in ice for 3 hours, and was then poured, with stirring, into a cold mixture of water and benzene. The benzene solution was separated and washed six times with ice water, dried with Drierite, and after a filtration, concentrated in vacuum. When crystals began to separate from the sirup during evaporation, ether was added and the crystalline product was collected on a filter. The first crop weighed 4.0 g, and an additional 0.7 g was obtained by concentrating the mother liquor. The acetylglycosyl halide was recrystallized at once by dissolving it in benzene and adding ether. Pentaacetyl-α-*d*-α-guloheptopyranosyl bromide crystallizes in slender

[6] The aldonic acid from which this sugar was prepared was originally named by La Forge, *d*-δ-guloheptonic acid. However, using the nomenclature for the heptoses suggested by Isbell [25], in which the alpha and beta represent not the order of discovery but the configuration of carbon 2, the acid is named *d*-α-guloheptonic acid, and the sugar *d*-α-guloheptose. The sugar used here was part of that originally prepared by Isbell [26].

prisms (fig. 2, *B*) which melt at 139° to 140° C and give $[\alpha]_D^{20} = -124°$. The new compound is fairly stable when pure, and has been kept at room temperature for several weeks in a shallow dish over sodium hydroxide. *Analysis:* Calculated for $C_{17}H_{23}O_{11}Br$: C, 42.25; H, 4.80; Br. 16.54. Found: C, 42.27; H, 4.92; Br, 16.47.

Since *d*-*α*-guloheptose has the *l*-talose configuration, a comparison of the molecular rotations of corresponding derivatives of the two sugars can be used for the assignment of ring structure and configuration. The following comparison of the molecular rotations of the new derivatives of *d*-*α*-guloheptose with the molecular rotations of the corresponding derivatives of talose prepared by Pigman and Isbell [21] may be used for this purpose:

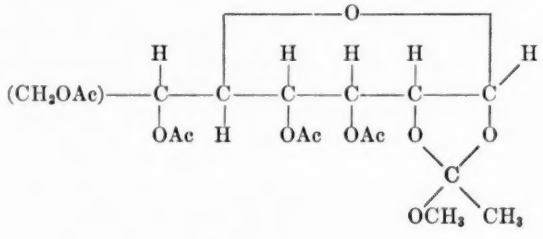
	[*M*]
Pentaacetyl-*α*-*l*-talose [7]	−27, 400
Hexaacetyl-*d*-*α*-guloheptose	−29, 000
Tetraacetyl-*α*-*l*-talosyl bromide [7]	−68, 100
Pentaacetyl-*d*-*α*-guloheptosyl bromide	−60, 000
Triacetyl-*l*-talose methyl orthoacetate [7]	−1, 340
Tetraacetyl-*d*-*α*-guloheptose methyl orthoacetate	+1, 400

[7] The molecular rotations of the *l*-talose derivatives have been obtained from those of the *d*-talose derivatives by reversing the signs.

The parallelism between the optical rotations of tetraacetyl-*d*-talosyl bromide and pentaacetyl-*d*-*α*-guloheptosyl bromide indicates that the two substances have like ring structures, and the same configuration for the glycosidic carbon. Unfortunately the structure of the tetraacetyl-*d*-talosyl bromide is not definitely established. However, it may be seen from the values given below that the "epimeric difference" [28] of the acetylglycosyl bromides of glucose and mannose and the epimeric difference of the acetylglycosyl bromides of galactose and talose are of the same order of magnitude. If the configurations ordinarily accepted for the acetylglycosyl bromides of glucose, mannose, and galactose are correct, tetraacetyl-*d*-talosyl bromide and pentaacetyl-*d*-*α*-guloheptosyl bromide have the alpha pyranose configuration, and the bromine atom of carbon 1 and the acetyl group of carbon 2 are *trans*.

	[*M*]	Epimeric difference
Tetraacetyl-*α*-*d*-glucopyranosyl bromide	+81, 300	27, 200
Tetraacetyl-*α*-*d*-mannopyranosyl bromide	+54, 100	
Tetraacetyl-*α*-*d*-galactopyranosyl bromide	+97, 200	29, 100
Tetraacetyl-*d*-talosyl bromide	+68, 100	

3. TETRAACETYL-*d*-*α*-GULOHEPTOSE METHYL 1,2-ORTHOACETATE



Two grams of powdered Drierite [8] and 4 g of freshly prepared silver carbonate were added to 50 ml of methyl alcohol, and the mixture was mechanically stirred in an ice bath for 10 minutes. One gram of finely powdered pentaacetyl-α-*d*-α-guloheptopyranosyl bromide was added, and the reaction mixture was mechanically stirred at 0° C for 44 hours. The solution was then filtered, and portions of the filtrate (10 ml) were pipetted into small glass-stoppered flasks for the analysis described below. When the solvent was evaporated from the remaining solution, the sirup crystallized almost completely upon the addition of a little ethyl alcohol with stirring. The crystalline material melted at approximately 100° C and gave no test for halogen.

In the analysis of the solution for orthoacetate, advantage was taken of the fact that 0.1 *N* acid at room temperature hydrolyzes both the ordinary acetyl and the orthoacetyl group, whereas 0.1 *N* alkali hydrolyzes the acetyl without disturbing the orthoacetyl group. The result of the acid hydrolysis corresponds to the sum of the methyl acetylglycosides and the orthoacetate, whereas the difference between the results obtained by acid and by alkaline hydrolysis is a measure of the amount of orthoacetate. Methyl pentaacetyl-*d*-α-guloheptoside gives 5 moles of acetic acid by either acid or alkaline hydrolysis, but tetraacetyl-*d*-α-guloheptose methyl orthoacetate gives 5 moles of acetic acid by acid hydrolysis and only 4 moles by alkaline hydrolysis. For analysis, the samples which had been transferred to small flasks were treated in the following manner:

Alkaline hydrolysis.—Fifty milliliters of 0.1 *N* barium hydroxide was added to a 10-ml sample of the solution in a glass-stoppered bottle, and the mixture was allowed to stand at 20° C for 3 hours. A back titration made with 0.1 *N* sulfuric acid showed that acid equivalent to 17.52 ml of 0.1 *N* barium hydroxide had been formed.

Acid hydrolysis.—Ten milliliters of 0.1 *N* sulfuric acid was added to a 10-ml sample of the solution, and the mixture was allowed to stand at 20° C for 24 hours. Fifty milliliters of 0.1 *N* barium hydroxide was then added, and at the end of 3 hours the excess alkali was titrated with 0.1 *N* sulfuric acid. The results showed that during the successive treatment with acid and alkali, acid equivalent to 21.95 ml[9] of 0.1 *N* barium hydroxide had been formed. If the material had been exclusively the orthoacetate, the requirement by alkaline hydrolysis would have been $21.95 \times 4/5 = 17.56$ ml. Actually 17.52 ml of 0.1 *N* alkali was required. Thus, within the error of measurement, the reaction product consists of the orthoacetate.

In a subsequent preparation of tetraacetyl-*d*-α-guloheptose methyl orthoacetate the analysis was omitted and the crystalline product, which separated upon evaporation of the methyl alcohol, was recrystallized several times from ethyl alcohol with the addition of petroleum ether. The compound, which crystallizes in chunky truncated prisms (fig. 2, *C*), is very soluble in ether and in alcohol but nearly insoluble in petroleum ether. When pure, tetraacetyl-*d*-α-guloheptose methyl 1,2-orthoacetate melts at 106° C and gives

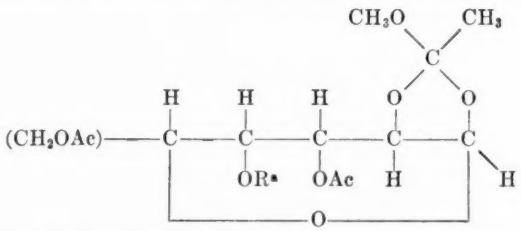
[8] In the course of the reaction, water is formed and reacts further to give objectionable byproducts. This factor was not taken into account until relatively recently when Helferich and coworkers used a desiccant to absorb the water as it was formed. Helferich, Bohn, and Winkler [29] used calcium chloride; and Reynolds and Evans [30] introduced the use of powdered Drierite (calcium sulfate), which was used in all of the Koenigs-Knorr reactions conducted in the course of this investigation.

[9] This value is somewhat higher than that (20.69 ml) calculated from the bromide used and the original volume of the solution. The higher value may be attributed to the evaporation of alcohol during filtration of the solution. However, the original concentration is unimportant, since the actual concentration is determined experimentally by the acid hydrolysis.

$[\alpha]_D^{20}=3.2°$. *Analysis:* Calculated for $C_{18}H_{26}O_{12}$: C, 49.77; H, 6.03. Found: C, 49.83; H, 6.09.

When treated with an anhydrous 0.1 *N* solution of hydrogen chloride in purified chloroform, the compound reacted rapidly in a manner characteristic of orthoesters [19]. Four minutes after dissolution the specific rotation was constant at −38.1°, whereas the specific rotation of the orthoacetate in chloroform is +3.2°. Upon evaporation, the solution gave a residue containing crystals, presumably pentaacetyl-*α*-*d*-*α*-guloheptosyl chloride, which is being investigated further. Since the compound was prepared by the method previously used for the preparation of the orthoacetate of rhamnose, in which the orthoester group has been shown to be united to carbons 1 and 2 [31], it is assumed that the orthoester group in this compound is also attached to carbons 1 and 2.

4. HEXAACETYLNEOLACTOSE METHYL 1,2-ORTHOACETATE



* R is the tetraacetyl-*β*-*d*-galactosyl group.

Five grams of heptaacetyl-*α*-neolactosyl chloride was used in the Koenigs-Knorr reaction under conditions identical with those described for pentaacetyl-*α*-*d*-*α*-guloheptosyl bromide, with the exception that the reaction time was increased from 44 hours to 72 hours. The methyl alcoholic solution, when evaporated in air to a sirup and stirred with a little ethyl alcohol, yielded slender prismatic crystals melting at 118° to 121° C and having a specific rotation of approximately +25°. Acid and alkaline hydrolyses of the reaction solution showed that only about 70 percent of the original sugar was present, and this was almost completely in the form of the orthoester. It was at first supposed that undissolved heptaacetyl-*α*-neolactosyl chloride remained in the silver residues, but by extraction of these residues with chloroform, a halogen-free sirup was obtained from which short rectangular crystals separated upon the addition of methyl alcohol. This crude material melted at 168° to 174° C and gave $[\alpha]_D^{20}=-13.7°$. It thus appeared that application of the Koenigs-Knorr reaction to heptaacetyl-*α*-neolactosyl chloride yielded, besides the crystalline orthoacetate, a second crystalline product, difficultly soluble in methyl alcohol and differing widely from the orthoacetate in optical rotation and melting point.

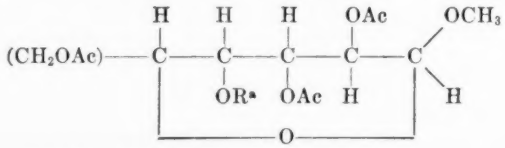
The hexaacetylneolactose methyl orthoacetate was recrystallized several times by dissolving it in absolute ethyl alcohol, concentrating the solution in vacuum to about one-third of its volume, and separating the crystals (slender prisms, fig. 2, *D*). When thoroughly dried, the compound melts at 121° to 122° C, whereas after air-drying, it usually melts several degrees lower. For the pure substance

$[\alpha]_D^{20} = +25.3°$. *Analysis:* Calculated for $C_{27}H_{38}O_{18}$: C, 49.84; H, 5.89. Found: C, 49.75; H, 5.77.

When the new compound was treated with an anhydrous 0.1 *N* solution of hydrogen chloride in purified chloroform, in agreement with the properties of other orthoesters [19], it was converted into the acetylglycosyl chloride. Four minutes after dissolution the specific rotation of the compound had changed from +25.3° to +62.7°. The solution, upon evaporation, yielded crystalline heptaacetyl-α-neolactosyl chloride, which was purified by recrystallization from ethyl acetate and identified by melting point and measurements of optical rotation.

Hydrolyses by acid and by alkali were carried out in approximately the same manner as that described for tetracetyl-*d*-α-guloheptose methyl orthoacetate. In the analysis of the crystalline compound, 0.2-g samples were dissolved in 10-ml quantities of methyl alcohol in glass-stoppered flasks and the hydrolyses were carried out on these solutions. By alkaline hydrolysis 0.2 g of hexaacetylneolactose methyl orthoacetate required 18.61 ml of 0.1 *N* alkali, and by acid hydrolysis 0.2 g of the compound was equivalent to 21.39 ml of 0.1 *N* alkali. Calculated for six acetyl groups, 18.45 ml of 0.1 *N* alkali; for seven acetyl groups, 21.52 ml of 0.1 *N* alkali.

5. METHYL HEPTAACETYL-β-NEOLACTOPYRANOSIDE



* "R" is the tetraacetyl-β-*d*-galactosyl group.

The second crystalline substance separated from the product of the Koenigs-Knorr reaction on heptaacetyl-α-neolactosyl chloride, melting point 168° to 174° C, was recrystallized several times from chloroform with the addition of ether, and finally from a large volume of methyl alcohol. When pure, methyl heptaacetyl-β-neolactoside forms rectangular prisms (fig. 2, *E*) which melt at 179° C and give $[\alpha]_D^{20} = -14.5°$. Unlike the orthoacetate, this compound did not react rapidly with hydrogen chloride. When it was treated with a chloroform solution of hydrogen chloride, there was no change in rotation, and the solution, after evaporation, yielded crystals identical with those of the original compound. *Analysis:* Calculated for $C_{27}H_{38}O_{18}$: C, 49.84; H, 5.89. Found: C, 49.70; H, 5.91.

Analysis by either acid or alkaline hydrolysis indicated seven acetyl groups. In the acid hydrolysis, a 0.2-g sample was equivalent to 21.64 ml of 0.1 *N* alkali; in the alkaline hydrolysis, to 21.66 ml of alkali. Calculated for seven acetyl groups, 21.52 ml of 0.1 *N* alkali.

Inasmuch as the hydroxyl on carbon 4 of the altrose unit of neolactose is blocked by a galactosyl group, the compound cannot be a furanoside and must be a pyranoside. The specific rotation of the beta modification of methyl heptaacetylneolactopyranoside may be calculated from the molecular rotations of pentaacetyl-α-*d*-altrose (+24,600) [27], octaacetyl-α-neolactose (+36,200) [23], and methyl tetraacetyl-β-*d*-altropyranoside (−22,100) [27]. According to the

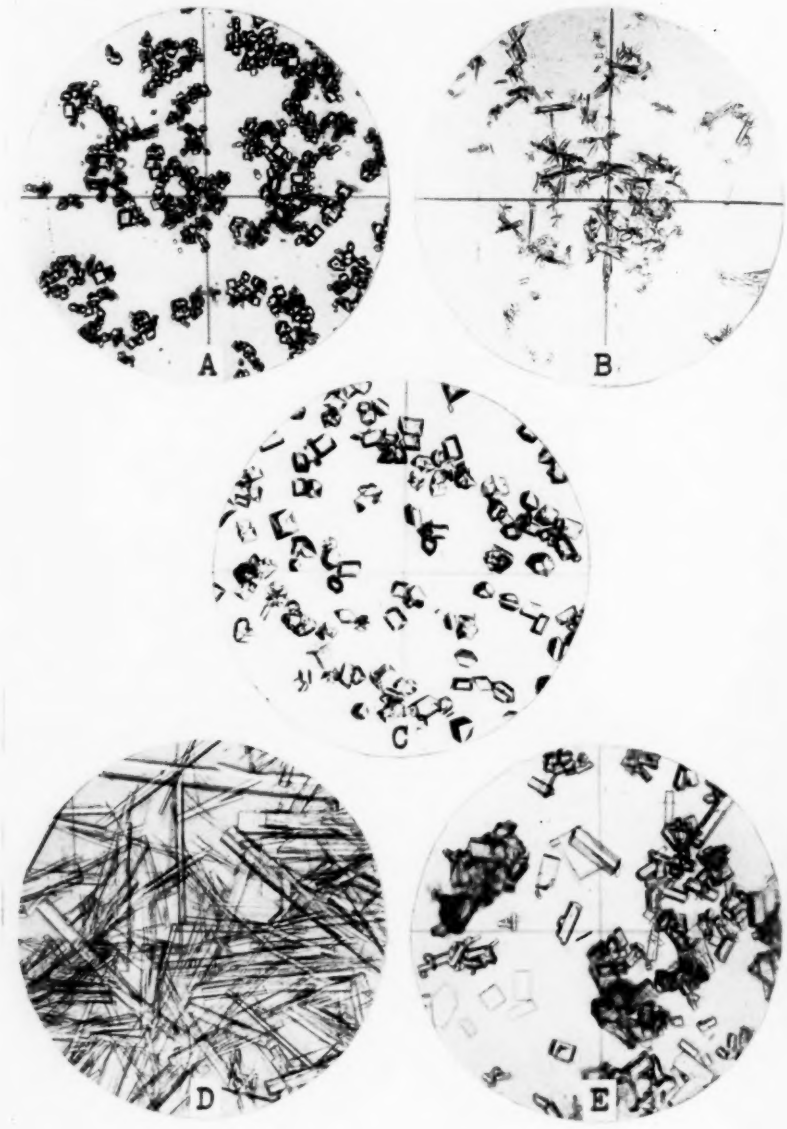


FIGURE 2.—*Photomicrographs of new compounds.*

A, Hexaacetyl-α-*d*-α-guloheptopyranose.
B, Pentaacetyl-α-*d*-α-guloheptopyranosyl bromide.
C, Tetraacetyl-*d*-α-guloheptose methyl 1,2-orthoacetate.
D, Hexaacetylneolactose methyl 1,2-orthoacetate.
E, Methyl heptaacetyl-β-neolactopyranoside.

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principle of optical superposition as applied to the sugars by Hudson, the difference in the molecular rotations of pentaacetyl-α-*d*-altrose (+24,600) and octaacetyl-α-neolactose (+36,200) should equal approximately the difference in the molecular rotations of methyl tetraacetyl-β-*d*-altropyranoside (−22,100) and methyl heptaacetyl-β-neolactopyranoside. Using the molecular rotations for the first three compounds, the molecular rotation of the fourth is calculated to be −10,500. This value corresponds to a specific rotation of −16.1°, which compares favorably with our experimental value of −14.5°, and therefore the compound is properly designated methyl heptaacetyl-β-neolactopyranoside.

V. SUMMARY

α-*d*-α-Guloheptose was acetylated by the low-temperature pyridine method to yield crystalline hexaacetyl-α-*d*-α-guloheptopyranose, melting point 126° C, $[\alpha]_D^{20} = -62.8°$. The new compound, when treated with hydrogen bromide in acetic acid, gave crystalline pentaacetyl-α-*d*-α-guloheptopyranosyl bromide, melting point 139° to 140° C, $[\alpha]_D^{20} = -124°$.

The mechanism of orthoester formation was discussed in light of the opposite-face concept for the Walden inversion, and a test of the mechanism was made by application of the Koenigs-Knorr reaction to the new pentaacetyl-α-*d*-α-guloheptopyranosyl bromide and to heptaacetyl-α-neolactosyl chloride. Both of these compounds have configurations which allow the acetyl group of carbon 2 to approach the face of carbon 1 opposite the replaceable halogen, and hence should yield orthoacetates according to the opposite-face hypothesis for the formation of orthoesters. On treatment with methyl alcohol in the presence of silver carbonate, pentaacetyl-α-*d*-α-guloheptopyranosyl bromide gave an almost quantitative yield of tetraacetyl-*d*-α-guloheptose methyl 1, 2-orthoacetate, melting point 106° C, $[\alpha]_D^{20} = +3.2°$. Heptaacetyl-α-neolactosyl chloride under like treatment gave about 70 percent of hexaacetylneolactose methyl 1,2-orthoacetate, melting point 121° to 122° C, $[\alpha]_D^{20} = +25.3°$, and about 30 percent of methyl heptaacetyl-β-neolactopyranoside, melting point 179° C, $[\alpha]_D^{20} = -14.5°$. Presumably these new compounds are formed, respectively, by an intramolecular orthoester reaction and by a competitive extramolecular glycosidic reaction. Since neolactose is a substituted altrose, and orthoesters of the altrose configuration have not heretofore been prepared, the formation of the orthoacetate is convincing evidence for the validity of the opposite-face mechanism, as previously postulated by one of the authors to explain orthoester formation.

The new orthoacetates show the reactions characteristic of the sugar methyl orthoacetates, including stability to alkaline hydrolysis and the formation of the normal glycosyl halide on treatment with hydrogen chloride. Tetraacetyl-*d*-α-guloheptose methyl orthoacetate, on treatment with hydrogen chloride, gave a crystalline material, presumably pentaacetyl-α-*d*-α-guloheptosyl chloride, which is being investigated further; and hexaacetylneolactose methyl orthoacetate yielded heptaacetyl-α-neolactosyl chloride.

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REFLECTION-TRANSMISSION RELATIONSHIPS IN SHEET MATERIALS

By Herbert F. Launer

ABSTRACT

Reflectances of transmissive sheets, calculated from the transmissions of one and two sheets, are compared with reflectances obtained by using the General Electric Recording Spectrophotometer. The expression used as a basis for calculation, $R_a = \sqrt{1-(T_a^2/T_{2a})}$, in which R_a is the reflectance, and T_a and T_{2a} are the transmissions of one and two sheets, respectively, of a, was derived by considering the infinite series of reflections undergone by light, or radiant energy in general, in passing through the two sheets. The expression was found to be valid and useful over a wide range of reflectances and wavelengths, for materials such as paper, glass, and an organic plastic.

The method is an absolute one, since it involves no reflectance standard. It involves no spherical or similar integrating device, nor does it involve any reflecting surface other than that of the sample itself, as a fundamental part of the measurements. When transmission values for diffuse incidence are substituted into the expression, the reflectances thus calculated correspond to the conditions of diffuse incidence and diffuse viewing, and as such are somewhat higher than the usual directly measured reflectances for normal incidence and diffuse viewing (or diffuse incidence and normal viewing). For clear sheets, with normal incidence, specular reflectance may be calculated.

The method thus affords a means of determining, from two simple measurements, the specular-plus-diffuse reflectance of transmissive sheets for diffused light or radiant energy in general.

The expression as derived is theoretically inapplicable to diffusing sheets for light of normal incidence, but a compensation of errors allows close agreement over the visible range, at 365 millimicrons, and for "white" light, for all except tissue paper and other materials of like transmissivity.

For diffuse incidence at 365, and to a certain extent, at 405 millimicrons, some papers show deviations from the simple theory because of fluorescence effects. This and other effects are discussed.

Reflectances in the infrared region near 850 millimicrons are also calculated but no standard for comparison is available for these values. The sources of errors at the shorter wavelengths, however, do not interfere in the infrared region.

Transmissions of papers were found to be dependent upon the angle of incidence.

Reflectances throughout the visible region, measured at 45° from normal incidence, were found to agree closely, for the type of papers studied, with those obtained using the General Electric Recording Spectrophotometer, which corresponds to the conditions of normal incidence and diffuse viewing.

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I. INTRODUCTION

In a current study of the photochemistry of paper it was necessary to determine the absolute total reflection and transmission factors of the sheets to permit calculation of the fractional light absorption. The measurement of transmission was relatively simple, but the determination of absolute reflectance, in, for example, the near infrared, for which no reflectance standard is available, led to a consideration of absolute methods. Gibson [1][1] and Van den Akker [2] have recently reviewed various phases of spectrophotometry, particularly with respect to the problems of the reflectance standards and geometrical design of instruments which yield values in terms of a standard magnesium oxide, or similar, surface. Taylor [3] has described an absolute reflectometer in which magnesium oxide (or similar) surfaces play a fundamental part in the measurement, but not in the calculation, of diffuse reflectance. No method, however, has been shown to yield absolute reflectance of diffusing materials, which does not involve, either explicitly or implicitly, the reflectance of either a standard or of the surface of an integrating sphere.

For transmissive materials in sheet form a method suggests itself for obtaining absolute reflectance without involving a standard or any other reflecting surface. Consider light, or radiant energy in general, passing through two sheets of any material, a, having the reflection and transmission factors R_a and T_a, corresponding to a definite kind of light. For unit incident flux, the light immediately after transmission by the first sheet has a flux equal to T_a. This light then undergoes an infinite series of reflections between the two sheets, so that the flux incident upon the second sheet is $T_a/(1-R_a^2)$, which after transmission through the second sheet becomes $T_a^2/(1-R_a^2)$. Equating this to T_{2a}, the transmission of the two sheets, and transposing, the following expression is obtained:

$$R_a=\sqrt{1-\frac{T_a^2}{T_{2a}}}. \tag{1}$$

If the two sheets differ, the expression becomes

$$R_aR_b=1-\frac{T_aT_b}{T_{ab}}. \tag{2}$$

[1] Figures in brackets indicate the literature references at the end of this paper.

Equation 1 was derived in its present form by Gurevich [4], and Smith [5] and in other forms by Stokes [6], Channon, Renwick, and Storr [7], and Ryde and Cooper [8], for diffusing materials, and by Benford [9] for sheets of glass. The expression, however, has apparently not been tested experimentally.

Gurevich assumed the expression to be valid and used it to calculate reflectances of some paper samples in heterogeneous light, but he presented no directly measured reflectances to allow a comparison. Also using heterogeneous light, Kubelka and Munk [10], Steel [11], and Judd [12] studied the relationships between reflectance, thickness, and scattering for papers and other diffusing materials.

The experimental verification of eq 1 is of interest for various reasons. Aside from the value of an absolute method based upon principles entirely different from those of existing methods, it would permit the determination of the reflectance of transmissive sheets from relatively simple transmission measurements, using inexpensive equipment and weak sources of light, without amplification in the measuring system since practically all of the transmitted light is to be measured directly.

In the present paper, reflectances obtained by direct measurement, for a variety of materials, at various wavelengths, are compared with reflectances calculated from transmission measurements of one and two sheets, using eq 1. Various factors causing deviations from the simple theory, such as changes in the values of R_a and T_a resulting from changes in spectral and geometric distribution of the light by the first sheet are discussed.

II. SAMPLES STUDIED

Six papers were selected for study which had been produced in the paper mill at the National Bureau of Standards from a wide variety of commercial materials to secure various representative types of papers. The data significant for the optical properties are listed in the tables; further details as to the papers may be obtained from the publication by Shaw and O'Leary [13]. Three widely differing commercial papers—namely, a tissue paper, a bluish-tint writing paper, and a heavily filled cigarette paper—were also studied. All of the papers had a matte finish. A relatively thick sheet of an organic plastic, a urea-formaldehyde laminated with very thin paper, was included in the investigation, as was a sheet of photographic plate glass.

III. APPARATUS

1. PHOTOELECTRIC EQUIPMENT

The photoelectric circuit used was that described by Brice [14]. Two General Electric "Light-Sensitive" cells were used, one of which measured the radiant energy transmitted by the sheets and the other of which compensated for lamp fluctuations. A galvanometer having a sensitivity of 0.5 μv/mm and a calibrated potentiometer of 100 ohms total resistance, capable of being read to the nearest 0.1-percent transmission, completed the circuit. With this arrangement transmission values could be estimated to the nearest 0.05-percent transmission.

The maximum flux density used corresponded to a photocurrent of 5 μa or less, thus making for conditions of highest accuracy, as found

by Brice. The apparatus was checked for accuracy by measuring the transmission of a polished glass, found by the Photometry and Colorimetry Section to transmit 16.0 percent at a certain wavelength, and by measuring the transmissions of two sectored disks transmitting 25.0 and 50.0 percent. The results showed that the probable error was less than 0.1-percent transmission.

The measuring cell was adapted for transmission measurements by removing the photosensitive selenium-covered steel plate from the hard-rubber case. The plate was mounted on a flat, hard-rubber surface, and the transmission samples were held under spring tension directly against the photosensitive surface by a flat metal frame, the opening of which was slightly larger than the photosensitive surface. Electric contact with the plate was made on the back by two springs extending through holes drilled in the hard rubber. On the front surface contact was made by thin (0.0005-in.) silver foil, two strips of which covered the roughened borders and were held under tension against them by the frame. Thus the spacing between the receiving surface and the transmission samples was actually 0.0005 in. under the frame.

For the experiments with diffuse radiant energy, a sheet of paper, No. 198, 20 by 20 cm, which was mounted 38 mm in front of the cell, 19 by 41 mm, used for transmission measurements, served as a diffusing screen. Multiple reflections between this screen and the sample being studied can be shown to introduce negligible errors into the calculated reflectances. The light source was placed at distances of 35 to 60 cm from the diffusing screen. For experiments with normal (perpendicular) illumination this diffusing screen was removed.

2. LIGHT SOURCES AND FILTERS

Spectrally homogeneous radiant energy was obtained by isolating mercury lines from a 400-watt, "high-intensity" glass-enclosed commercial mercury-vapor lamp. The far red, infrared, and "short" ultraviolet regions were removed by a 15-mm thickness of 0.117 molar $CuCl_2 \cdot 2H_2O$ (2 percent) solution in a glass cell. Using this filter with the following glass filters, various Hg lines were isolated, respectively: Corning 986 (7 mm), 365 mμ; Corning Noviol O and 597, 405 mμ; Noviol A and 585, 436 mμ; Jena OG1, Corning 512, and Corning G584J, 546 mμ; Jena RG1, 623 mμ. The light thus isolated was not perfectly homogeneous in all cases. As an example, the bright 436 line was faintly contaminated with the 492 line, but not sufficiently so as to affect the results seriously. In no case, however, did the red and infrared, also transmitted by the Corning filters Nos. 986, 597, and 585, correspond to more than 0.05 percent of the cell response. For "white" light a 110-volt, 100-watt tungsten incandescent lamp, in combination with the cupric chloride filter, was used. For the infrared, a 110-volt, 1,000-watt "Airway Beacon" incandescent lamp, in combination with a Corning 254 filter and a 15-mm layer of water, was used. The effective wavelength of the infrared thus isolated was approximately 850 mμ, calculated as the spectral centroid from the spectral distribution of the lamp (maximum at 900 mμ), the transmission of the filter, and the spectral sensitivity of the cell (manufacturers' data).

IV. EXPERIMENTAL RESULTS AND THEORETICAL DISCUSSION

1. METHODS OF DIRECT MEASUREMENT OF REFLECTANCE

The test of eq 1 consists in comparing reflectances calculated from transmission values with directly measured reflectances. The values obtained by using the General Electric Recording Spectrophotometer, which employs the principle of normal incidence and diffuse viewing, were adopted as the basis for all of the directly measured reflectances. Not all of the reflectances were obtained in this manner, but the results obtained by an alternate method were found to be the same, within the limits of the experimental errors of both methods, for the papers included in this study.

The alternate method was the familiar one of normal incidence and 45° viewing. Light of the desired wavelength was focused on the paper or standard MgO surface to give an image of 2 by 4 cm. A General Electric cell to receive reflected light was mounted at a distance of 15 cm from the light spot. Another cell, illuminated by reflection from a piece of clear glass placed at an angle in the incident beam, compensated for lamp fluctuations, as previously described. The MgO surface was freshly deposited to approximately ¾-mm thickness on a slab of duralumin held in the smoke of burning magnesium ribbon.

The values obtained by using these two direct methods are compared in table 1 for part of the papers included in this study. Parts of the same sheets, but not identical areas thereof, were measured in both cases. The agreement, however, is seen to be satisfactory, and independent of the wavelengths studied. Since both methods yield values relative to MgO, the reflectances were converted to absolute ones by the use of Preston's [15] factors for MgO.

TABLE 1.—*Comparison between reflectances of papers obtained from curves using the General Electric Recording Spectrophotometer, and those obtained by measuring reflectances at 45° fron normal incidence*

Paper No.	Reflectances at—							
	405 mμ		436 mμ		546 mμ		623 mμ	
	G. E.	45°	G. E.	45°	G. E.	45°	G. E.	45°
	%	%	%	%	%	%	%	%
1215	76.9	77.1	78.6	78.1	81.2	81.2	81.2	81.2
1214	66.5	65.6	69.5	69.9	73.6	74.2	73.8	73.1
1191	73.2	73.6	75.8	75.8	79.3	79.6	79.7	78.7
1170	63.0	62.4	67.9	67.3	73.2	73.2	73.6	72.2
1133	50.5	50.4	56.2	57.6	65.9	66.8	68.2	67.4
1136	54.6	55.6	61.4	62.5	71.9	72.9	74.1	73.7

The spectrophotometer values at the wavelengths 405, 436, 546, and 623 mμ were taken from curves obtained by H. J. Keegan, of the Photometry and Colorimetry Section, for samples Nos. 1215, 1214, 1191, 1170, 1133, 1136, and 200. The values were reduced in the manner described by Gibson and Keegan [16]. All other reflectances were determined by the alternate method, with the exception

of that of the glass, which was calculated from the refractive index $n=1.5157$ obtained by C. A. Faick, of the Glass Section, for yellow light.

2. EFFECT OF REFLECTANCE OF THE MEASURING CELL

In measuring the transmission of sheets held very close to the photosensitive surface, the small amount of radiant energy reflected by this surface must be taken into account. This may be done by considering separately the optical relationships involved for one and two sheets. By summing up the infinite series of reflections between one sheet and the cell surface, the following expression is obtained:

$$T_a=t_a(1-R_aR_c). \tag{3}$$

Similarly, for two sheets:

$$T_{2a}=\frac{t_{2a}(1-R_aR_c)}{1+t_{2a}R_aR_c}, \tag{4}$$

where T_a and T_{2a}=corrected transmissions of one and two sheets, t_a and t_{2a}=measured transmissions of one and two sheets, and R_a and R_c=reflectances of the sheet and the cell.

Equations 3 and 4 are then substituted into eq 1 and the following complete expression is obtained:

$$R_a=\sqrt{\left(1-\frac{t_a^2}{t_{2a}}\right)\left(\frac{1}{1-t_a^2R^2{}_c}\right)+\left[\frac{R_c}{2}\left(\frac{t_a^2}{t_{2a}}\right)\frac{1-t_{2a}}{1-t_a^2R_c^2}\right]^2}+\frac{R_c}{2}\left(\frac{t_a^2}{t_{2a}}\right)\frac{1-t_{2a}}{1-t_a^2R_c^2}. \tag{5}$$

For usual values of R_c (near 0.1) eq 5 may be simplified by omitting negligible terms:

$$R_a=\sqrt{1-\frac{t_a^2}{t_{2a}}}+0.002+\frac{1}{2}R_c\left(\frac{t_a^2}{t_{2a}}\right)(1-t_{2a}). \tag{6}$$

The figure 0.002 applies for most papers but reaches a value of 0.004 for the more transmissive diffusing sheets.

For materials having low transmissions, as do some papers in the ultraviolet and violet, t_{2a} becomes very small, less than 0.01, and the errors correspondingly large. To avoid this, a more transmissive, auxiliary sheet may be used in combination with the sheet to be measured, instead of two sheets of the same material. For this case, eq 2 is used and becomes

$$R_b=\frac{1}{R_a}\left(1-\frac{T_at_b}{t_{ab}}\right), \tag{7}$$

where R_a=reflectance of auxiliary sheet, as calculated from eq 6, or otherwise known;

T_a=corrected transmission of auxiliary sheet, calculated from eq 3;

t_b=measured transmission of sheet whose reflectance is being determined; and

t_{ab}=measured transmission of the combination, with sheet b between a and the cell.

TABLE 2.—*Reflectances, calculated from the transmissions of one and two sheets, compared with the reflectances directly measured with the Electric Recording Spectrophotometer*

TABLE 2.—*Reflectances, calculated from the transmissions of one and two sheets, compared with the reflectances directly measured with a General Electric Recording Spectrophotometer [a] and other equipment*

Number and type of sheet material	Reflectances at—																			
	623 mμ			546 mμ			436 mμ			405 mμ			365 mμ			Infrared [b]		Heterogeneous ("white") light [c]	
	Direct measurement	Calculated from transmissions		Direct measurement	Calculated from transmissions		Direct measurement	Calculated from transmissions		Direct measurement	Calculated from transmissions		Direct measurement	Calculated from transmissions		Calculated from transmissions		Direct measurement	Calculated from transmissions
	Normal incidence	Normal incidence	Diffuse incidence	Normal incidence	Normal incidence	Diffuse incidence	Normal incidence	Normal incidence	Diffuse incidence	Normal incidence	Normal incidence	Diffuse incidence	Normal incidence	Normal incidence	Diffuse incidence	Normal incidence	Diffuse incidence	Normal incidence	Normal incidence
1215 [d]—rag paper; 14% $CaCO_3$ filler; 0.0036" thickness	% 81.2	% 80.7	% 81.8	% 81.2	% 81.4	% 82.4	% 78.6	% 78.3	% 80.5	% 76.9	% 77.3	% 79.9	% 73.2	% 73.9	% 78.2 (72.6)	% 76.7	% 76.9	% 80.6	% 81.4
1214—rag paper; no filler; 0.0038" thickness	73.8	72.6	74.7	73.6	73.1	74.7	69.5	68.1	69.8	66.5	65.6	67.1	60.8	61.0	66.3 (57.8)	69.7	69.9	73.9	73.3
1191—rag paper; 14% clay filler; 0.0036" thickness	79.3	78.8	80.2	79.3	79.5	80.9	75.8	75.2	77.6	73.2	73.7	75.8	68.2	69.8	75.8 (65.9)	76.0	73.9	79.2	79.7
1170—wood pulp paper; 14% clay filler; 0.0034" thickness	73.6	72.8	74.1	73.2	72.7	74.4	67.9	66.0	69.0	63.0	63.7	65.9	54.2	53.0	66.7 (48.9)	68.1	66.9	73.0	72.7
1133—yellowish wood pulp paper; no filler; 0.0035" thickness	68.2	66.6	70.3	65.9	63.9	68.1	56.2	52.1	56.7	50.5	51.5	53.4	41.6	38.0	54.8 (37.4)	66.0	67.2	66.5	65.8
1136—yellowish wood pulp paper; 9% clay filler; 0.0037" thickness	74.1	73.1	76.2	71.9	71.2	73.9	61.4	60.5	62.7	54.6	55.1	67.0	46.4	46.8	74.0 (58.6)	70.8	71.9	72.8	72.8
128—bluish tint rag bond paper; 0.004" thickness	66.7	66.6	69.8	67.7	67.6	69.8	67.6	64.9	68.6	64.4	62.9	66.6	61.2	60.1	64.0 (60.4)	61.9	63.3	67.9	66.4
1002—cigarette paper; 19% $CaCO_3$ filler; 0.0015" thickness	60.9	59.8	63.6	61.9	61.5	64.2	62.5	62.2	65.2	62.6	61.6	64.6	60.1	60.1	62.4 (62.0)	51.6	51.4	61.5	62.4
198—facing tissue; 0.001" thickness	37.7	32.1	40.3	39.4	34.9	40.9	40.2	33.0	40.9	38.6	29.0	37.6	35.2	16.7	33.7	24.3	29.5	39.0	32.2
200—"thick" organic plastic; 0.023" thickness	34.2	[e] (u. v.)	36.9	36.1	(u. v.)	37.9	35.1	(u. v.)	33.8	28.1	(u. v.)	30.4	.....	.....	.....	(u. v.)	28.5	.....	.....
202—clear glass plate; 0.047" thickness				[f] 8.1	7.8	11.5													

[a] Used for values at 623, 546, 436, and 405 mμ for samples 1215, 1214, 1191, 1170, 1133, 1136, and 200. See text for details.

[b] Wavelength approximately 850 mμ. See text for details.

[c] Heterogeneous light was that from a 100-watt, 110-volt tungsten lamp, after transmission through a 15-mm layer of 0.117 *M* cupric chloride solution.

[d] The first 6 papers were made in the Bureau paper mill [13]. Nos. 128 and 198 were standard samples of the same number from the Government Printing Office. The papers were near-white or neutral gray unless otherwise specified.

[e] "u. v." stands for "unreal value," since the expression $1-(t^2_a/t_{2a})$ had a negative value in these cases.

[f] Reflectance was calculated from the refractive index for yellow light, $n=1.5157$.

TABLE 3.—*Transmission*[a] *data for the sheet materials*

Number of sheet material	Transmissions at—											
	Infrared		623 mμ		546 mμ		436 mμ		405 mμ		365 mμ	
	t_a	t_{2a}	t_a	t_{2a}	t_a	t_{2a}	t_a	t_{ab} or t_{2a}	t_a	t_{ab} or t_{2a}	t_a	t_{ab} or t_{2a}
1215	0.244	0.136	0.167	0.078	0.153	0.067	0.114	0.0575	0.096	0.042	0.069	0.023
1214	.303	.170	.229	.111	.212	.095	.157	.068	.127	.047	.083	.024
1191	.257	.137	.173	.078	.158	.067	.111	.0535	.087	.036	.051	.0165
1170	.334	.192	.250	.130	.227	.109	.158	.0675	.118	.043	.062	.018
1133	.339	.199	.270	.136	.240	.101	.148	.0545	.107	.034	.0585	.015
1136	.283	.157	.213	.101	.187	.073	.104	.041	.065	.024	.0285	.009
128	.363	.210	.292	.158	.279	.143	.240	.104	.2185	.0815	.1765	.0504
1002	.488	.313	.370	.219	.347	.198	.304	.150	.277	.126	.2395	.090
198	.687	.510	.582	.394	.556	.364	.494	.287	.460	.241	.392	.170
200	.624	.418	.586	.390	.555	.352	.419	.195	.274	.081	.033	.009
202					{.9260 b. 9285	.868 b. 867						

[a] Measured transmissions of diffusely incident radiant energy for 1 sheet are given as t_a, for 2 sheets of the same material as t_{2a}, and for the combination of the various materials with No. 128 as t_{ab}. This last combination was used for the first 6 papers at 436, 405, and 365 mμ. See text for further details.

[b] These values were obtained with light of normal incidence.

All of the calculated reflectances (reflectances calculated from transmissions) in table 2 were obtained by substitution of the measured transmissions, some of which are given in table 3, into eq 6 or 7. These data will be analyzed in following sections as to significance and pertinent factors. Equation 7 was used for reflectances at 436, 405, and 365 mμ for papers 1215, 1214, 1191, 1170, 1133, and 1136, using paper 128 as sheet *a*. For all other cases t_{2a} was feasibly large (greater than 0.05) and the reflectances were calculated by means of eq 6. At 623 and 546 mμ the values calculated with both equations for the first six papers agreed well without any noticeable trend.

The reflectance, R_c, of the lacquered gold-selenium receiving surface of the General Electric cell was obtained as follows: Since the images reflected by the cell surface were fairly regular, R_c was determined relative to a piece of Corex-*D* glass. A beam was so focused, by means of a lens, that after 10° incidence upon the cell surface and reflection at 10°, the image was projected upon the center of another cell which measured the intensity of the reflected beam. A third cell was used to compensate for intensity fluctuations. By repeating the measurement with a piece of Corex-*D* glass at various wavelengths, the following ratios of R_c to $R_{\text{Corex-}D}$ were obtained, for the indicated wavelengths: 365 mμ, 0.85; 436 mμ, 0.92; 578 mμ, 0.96; 623 mμ, 1.0; infrared, 1.27. Two other cells gave essentially the same reflectance ratios.

From the reflectance of the Corex-*D* glass, 0.085 (manufacturer's data), the reflectance of the cell surface for normal incidence may be calculated. The use conditions of the cell are such, however, that the reflectance for diffuse incidence should be used for R_c. The values of R_c for normal incidence represent minimum values; maximum values may be obtained by weighting, from $\theta=0$ to $\theta=\pi/2$, the values of the reflectances of the cell for various angles of incidence.

The relationship between R_c and angle of incidence, θ, was found in the following way: A small spot of light of wavelength 578 mμ was focused on the surface of the cell, which could be rotated through known angles. The cell circuit was balanced against the compen-

sating cell for normal incidence, and readings were then taken of the cell response at the various angles in terms of that for normal incidence. From this the variation in R_c with θ, angle of incidence, could be computed, based upon R_c at normal incidence, 0.082, for this wavelength. The values are recorded in table 4.

TABLE 4.—*Reflectance of receiving surface, R_c, of light-sensitive cell as a function of the angle of incidence, θ, at 578 mμ*

θ	R_c	θ	R_c
Degrees		*Degrees*	
0	0.082	40	0.088
10	.082	50	.097
20	.083	60	.118
30	.084	70	.146

From the data in table 4, and from the reasonable assumption that $R_c=0.2$ at $\theta=80°$, which value is not heavily weighted in any case, the reflectance of the cell for completely diffused illumination may be computed, using the method described by McNicholas [17], and applied by Judd and Gibson [18] to a similar problem; by

$$R_{c(\text{diffused})}=\frac{\sum_0^{\pi/2} R_\theta \sin 2\theta}{\sum_0^{\pi/2} \sin 2\theta}=0.107. \tag{8}$$

This value represents the upper limit corresponding to completely diffused illumination, which is, in general, not attained.

Great accuracy in the value for R_c is, however, not necessary, inasmuch as the correction factor, $\frac{1}{2}R_c(t_a^2/t_{2a})(1-t_{2a})$, usually contributes less than 2 percent in eq 6. For the present purposes, therefore, the value 0.09, somewhat less than intermediate between the two extremes, was adopted for R_c at 578 mμ. This led to the following values for R_c at the other wavelengths: 365 mμ, 0.08; 436 mμ, 0.085; 623 mμ, 0.095; 850 mμ, 0.12. These values were used in eq 6 and in the calculations of T_a in eq 7.

3. CALCULATED REFLECTANCES FOR DIFFUSE AND NORMAL INCIDENCE

The two sets of calculated reflectance values in table 2 correspond to the two types of illumination used, namely diffuse and normal incidence, although it should be noted that even in the latter case the second sheet of a combination is illuminated diffusely to the extent that the first sheet acts as a diffuser. The transmission values for diffuse incidence are given in table 3; those for normal incidence were omitted for the sake of brevity.

As it was pointed out previously, the directly measured reflectances were intended to serve as a standard of comparison for the calculated reflectances. Such a comparison is strictly valid only if the geometrical conditions involved in both cases are identical. This is, however, not the case in the present work, inasmuch as the directly measured reflectances correspond to the condition of normal incidence and diffuse viewing (or, what is numerically the same for the papers, normal

incidence and 45° viewing), whereas the calculated reflectances correspond to the condition of diffuse incidence and diffuse viewing. The latter condition obtains, to a varying extent, in the transmission measurements with normal incidence, but the reflectances calculated therefrom involve errors which will be discussed subsequently.

It is not to be expected, however, that the values corresponding to the two sets of geometrical conditions should be greatly different. McNicholas [17], using diffuse incidence (undispersed incandescent-lamp light), computed that the diffuse reflectances of a variety of matte materials were, in general 1- to 3-percent reflectance higher than reflectance in the direction normal to the surface, which latter condition is equivalent to normal incidence and diffuse viewing, according to the Helmholtz reciprocity relation.

The samples studied by McNicholas were opaque or mounted on opaque backings, and had surface characteristics different from those of matte papers. It was found, however, that the materials of the present study behave similarly. This can be seen, although indirectly, from a comparison of the transmissions of various typical papers for normal and diffuse incidence, given in table 5, in which the first and last values in each column are to be compared in the present connection.

TABLE 5.—*Transmission of papers as a function of angle of incident light at 578 mμ*

θ	Measured transmissions (t_a)		
	Paper 198	Paper 1133	Paper 1215
Degrees			
0	0.607	0.268	0.160
10	.600	.264	.158
20	.589	.256	.154
30	.569	.243	.148
40	.547	.228	.141
50	.528	.213	.134
55	.518	.206	.131
60	*.517	*.202	*.129
70	.542	.203	.132
80	.680	.241	.156
Diffused	.569	.242	.150

* The increases in t_a with θ at angles greater than 60° are reproducible but probably do not represent real characteristics of papers. They are apparently the result of the particular method of measurement, which consisted in varying the angle of the measuring cell and balancing the circuit at each angle with no paper. Beyond 60° the specular reflectance of the bare cell surface appears to increase much more rapidly with θ than that of the paper, so that the cell response per unit of radiant flux is greater with than without the paper. At angles below 60°, however, such an effect would be negligible, since the reflectance of the cell changes only slightly with θ at the smaller angles.

The results in table 2 show that the reflectances calculated from transmissions for diffuse incidence are higher than the directly measured reflectances by 1- to 3-percent reflectance, except in the extreme violet and ultraviolet, where the differences are, in general, much greater, and will be shown to be due to fluorescence effects. The values in parentheses for 365 $m\mu$ demonstrate the general result of correcting for fluorescence.

The reflectances, calculated from transmissions for normal incidence, are seen to be in good agreement with the directly measured reflectances, with the exception of the tissue paper, 198, and the organic plastic, 200, for which agreement is very poor, especially in the case of 200, for which no real values could be calculated. This is explained by the fact that the values for t_a for these sheets are much higher for

normal than for diffuse incidence (as shown in table 5) and are raised to the second power, whereas the corresponding values for t_{2a}, which enter eq 1 to the first power, are more nearly equal, since the second sheet of the combination is illuminated diffusely to a greater or less extent, by the first sheet. Thus, for normal incidence, the expression $1-(t_a^2/t_{2a})$ assumes low or even negative values for very transmissive sheets, but for most papers yields values which are just sufficiently low to be in fortuitous agreement with directly measured reflectances.

The departure from the simple theory, when normal incidence is used, is thus seen to be due to a change in the value of T_a as a consequence of the change in geometrical distribution of the radiant energy in passing through the first sheet.

This effect occurred in all cases in normal incidence, except for the clear glass, but it was less pronounced for the thicker or more diffusing papers, since such sheets exhibited less difference in t_a for normal and diffuse incidence. Furthermore, the mathematical form of eq 1 is such that its value is much less sensitive to this type of effect for sheets of high or medium reflectance than for sheets of low reflectance.

Another effect of using normal incidence, tending to compensate the one just discussed, arises from the fact that the photosensitive surface of the measuring cell has a smaller response for diffused light, as transmitted by papers, than for an equal flux of normally incident light. Since the photoelectric circuit was balanced at 100-percent transmission with no paper, the light was perpendicularly incident; but in a measurement with a diffusing material the light was at least partially diffused. Thus for normal incidence all values for t_a and t_{2a} were too low by the same fractional amount, leading to higher values for R_a.

Another effect which tended to give high values for R_a was that of fluorescence, as will be shown later in section 5.

The fact that good agreement is obtained between the reflectances calculated from transmission values for normal incidence and the directly measured reflectances is of practical rather than theoretical interest, inasmuch as this agreement is due to a compensation of errors.

The experiments with the glass sample, 202, aside from demonstrating the validity of eq 6 for very low reflectances, also show that valid results are obtainable for normally incident light as long as its geometric distribution is not altered in passing through the first sheet.

R_a for the glass for diffused light is higher than for normal incidence. This is in agreement with the theoretical conclusions of Judd and Gibson [18], who present data, obtained in another manner, from which it may be calculated that the glass they used had a reflectance of 12.6 percent for diffused light. It should be pointed out, however, that the present method does not lend itself to precision at these low reflectances owing to the form of the expression.

4. EFFECT OF THICKNESS OF SHEETS

In the case of the relatively thick organic plastic sheet, 0.023 in., an appreciable quantity of light may be lost edgewise. If x is the fraction of light *not* lost edgewise, in each sheet, then xT_a will enter the numerator in eq 1, and x^2T_{2a} will enter the denominator. Since the former is then squared, it is obvious that x cancels and that this type of loss does not invalidate eq 1.

Two other types of side losses are conceivable; one between the sheet or sheets and the cell, and the other between the two sheets. It can be shown that the former effect tends to raise the calculated reflectances and the latter tends to lower them. They thus tend to compensate and with the present experimental arrangement were probably negligible.

5. EFFECT OF FLUORESCENCE

The effect of fluorescence upon directly measured paper reflectance was studied at the Institute of Paper Chemistry [19], where it was found that large amounts of near infrared fluorescence arose from papers illuminated with incandescent-lamp light. In the present study, however, very little effect from infrared fluorescence should be noted, since this type of cell used is only about one-thirtieth to one-fiftieth as sensitive to infrared as to visible energy.

The papers included in the present study, however, were found to fluoresce markedly in the visible region when illuminated with 365-mμ, ultraviolet. This was determined as follows. The circuit previously described for measuring transmissions was used. A filter which had a spectral transmission of practically zero at 365 mμ, but which transmitted rather freely at longer wavelengths, was placed between the illuminated sheet or sheets and the measuring cell. Thus only fluorescent energy was measured.

Not all of the fluorescent energy was measured, however, since the filter, whose spectral characteristics are given in a footnote of table 6, had an average energy transmission of about one-half in the visible region. Therefore, the measured values for fluorescent energy for each sheet of paper, and for the combinations of the various sheets with a sheet of paper 128, were multiplied by a factor of 2, since additional experiments (data not given) with other filters, which cut off at various longer wavelengths, showed that the fluorescent energy was approximately equally distributed over the visible region. The corrected values are shown in table 6.

The values for fluorescence thus obtained are obviously included in the values for t_a and t_{ab} or t_{2a} at 365 mμ in table 3. When the latter are corrected for fluorescence and when the corrected transmissions are substituted into eq 7 (or eq 6 for papers 128 and 1002), the values for calculated reflectance for diffuse incidence are in better agreement with the directly measured reflectances than when fluorescence is not considered. The recalculated reflectances are given in parentheses in table 2. The calculated reflectances for normal incidence were not corrected, since fluorescence is one of the compensating factors resulting in fortuitous but useful agreement with directly measured reflectances.

For papers of very low transmission, however, this method does not yield dependable values for reflectance in regions causing fluorescence, owing to the fact that inaccuracies in the values for fluorescence lead to magnified errors in reflectance if the values for t_{ab} or t_{2a} are very small. When t_{ab} or t_{2a} is 0.04 or larger, however, fluorescence has only small or negligible effects upon the calculated reflectances. Thus, eq 6 or 7 may be used for calculating the reflectances of papers such as 128, 198, or 1002 in the 365-$m\mu$ ultraviolet with only small errors caused by neglecting the fluorescence.

TABLE 6.—*Fluorescence of papers caused by 365-mμ ultraviolet*

Number of paper	Fluorescent light,[a] expressed in transmission units[b]	
	1 sheet	1 sheet plus paper 128
1215	0.002	0.003
1214	.004	.004
1191	.002	.003
1170	.006	.005
1133	.006	.004
1136	.005	.003
1002	.003	.003
128	.007	.007

[a] The ultraviolet incident upon the papers was excluded from the measurements by means of a 10-mm layer, contained in a glass cell, of 0.65 molar cupric chloride solution at 26° C, which has the following transmittances (unpublished data): at 365 mμ, 0.0005; at 405 mμ, 0.176; at 436 mμ, 0.738; at 546 mμ, 0.788; at 578 mμ, 0.447; at 623 mμ, 0.041; at 691 mμ, 0.005; at 750 to 1400 mμ, 0.000.

[b] The values in this table are expressed in the same units as those of table 3 and thus may be subtracted directly from the values for t_a, t_{ab}, or t_{2a} to obtain the corresponding transmission values for the incident ultraviolet.

6. RESULTS OBTAINED BY USING HETEROGENEOUS ("WHITE") LIGHT AND INFRARED

The spectral distribution of heterogeneous ("white") light is usually altered by selective absorption in passing through a sheet of paper. This renders eq 1 theoretically inapplicable for such light, inasmuch as T_a and R_a may be changed by the first sheet. It was of interest from a practical standpoint, however, to determine the extent to which eq 1 could nevertheless be relied upon under these conditions. The reflectances in table 2 for normally incident heterogeneous light were calculated by using eq 6. A comparison with the directly measured reflectances shows that eq 1 is very useful for such measurements, except for very transmissive papers, such as 198, for which diffuse incidence must be used.

No comparison with directly measured reflectances was possible in the infrared, inasmuch as no standard of diffuse reflectance for the infrared is available, and inasmuch as the photoelectric responses in this region were too weak for unamplified measurement of reflectance, although they sufficed for measurement of transmission.

It should be noted, however, that the two principal causes for departure from the simple theory, namely fluorescence and change in geometric distribution during transmission, are not expected to be appreciable in the infrared. Errors due to fluorescence would necessarily be very small in this region for a variety of reasons, and the slight effect of changing the geometric distribution is evident from the results in table 2.

The writer takes pleasure in acknowledging the advice and comments of Deane B. Judd, of the Photometry and Colorimetry Section.

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WASHINGTON, September 16, 1941.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1431

Part of Journal of Research of the National Bureau of Standards, Volume 27, November 1941

STRESSES IN A RECTANGULAR KNEE OF A RIGID FRAME

By William R. Osgood

In Research Paper RP1130 [1] of the National Bureau of Standards a theoretical analysis has been presented of the stresses in a rectangular knee of a rigid frame. This analysis is not free from objection because in the limit, as the cross-sectional areas of the flanges approach zero, a

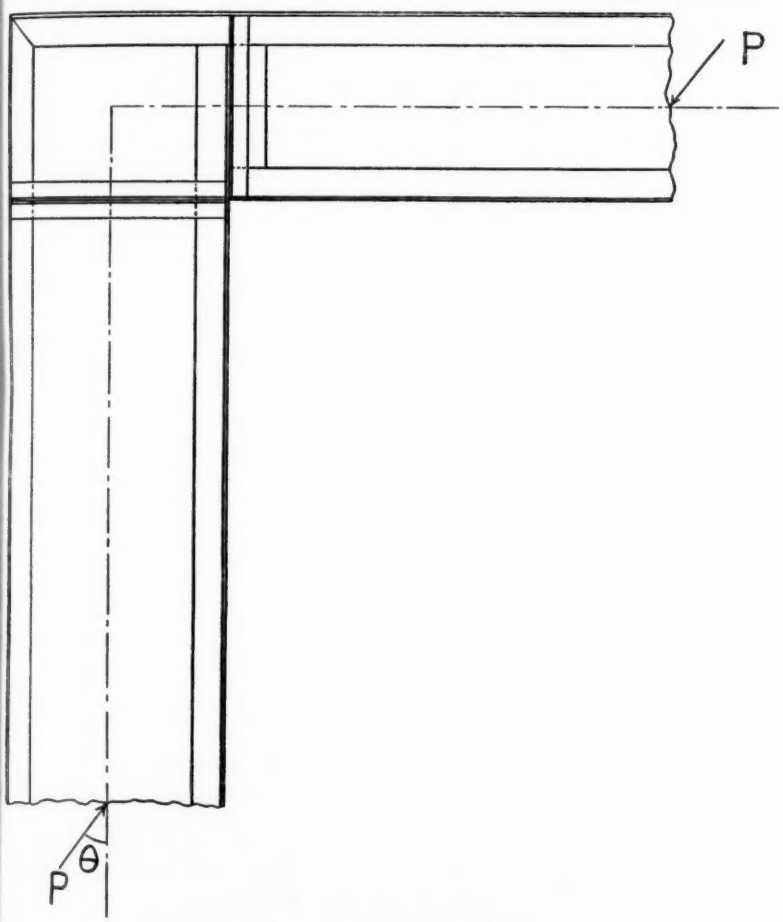

FIGURE 1.—*Corner of a rigid frame.*

[1] J. Research NBS, **21**, 269 (1938), RP1130.

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distribution of stress at the boundaries of the knee is approached which departs widely from what appears reasonable. In the present paper an analysis that is largely free from this objection is presented for a knee with two planes of symmetry.

Figure 1 shows in outline a corner of a rigid frame having a rectangular knee, and figure 2 shows an idealized conception of a frame

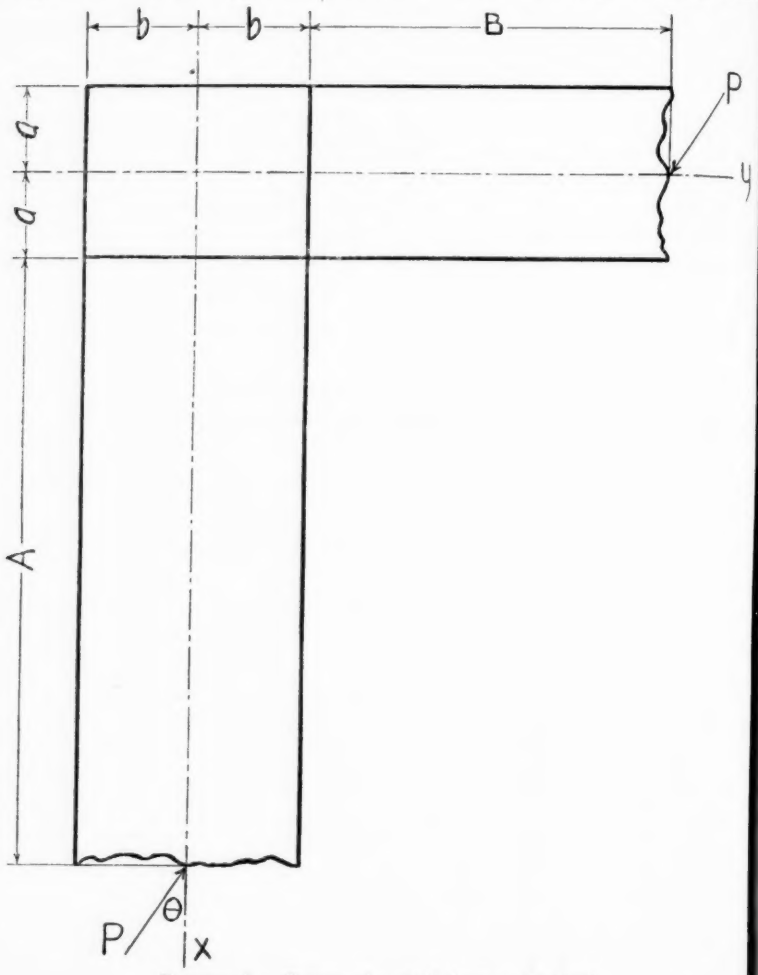

FIGURE 2.—*Corner of a rigid frame, idealized.*

in which the flanges are to be thought of as concentrated along their centroidal axes. It is assumed that the upper and lower flanges of the knee have the same cross-sectional area and the right and left flanges have the same cross-sectional area. Let us isolate the knee and consider the forces acting on it, figure 3 (a). In this figure

$$H=P \sin \theta,$$
$$V=P \cos \theta,$$
$$M_0=H(A+a)=V(B+b).$$

where P, A, B, a, b, and θ are the known quantities shown in figure 2. The system of forces shown in figure 3 (a) may be resolved into the three systems, each in equilibrium, shown in figure 3 (b), (c), and (d). If it is borne in mind that the forces H and V and the couples Ha, Vb, and M_0 are transmitted to the knee by the legs, in which the distribution of normal stress on a cross section is linear, except possibly in the immediate neighborhood of the knee, then it is reasonable to assume that the normal forces H and V are the resultants of uniformly distributed forces, and Ha, Vb, and M_0 the resultants of approximately uniformly varying forces. Under these assumptions, solutions may be obtained that satisfy the equations of equilibrium and the conditions of compatibility for the three cases of figure 3 (b), (c), and (d). In these solutions, which follow, the origin of coordinates is taken at the center of the knee and the coordinate axes parallel to the sides, as shown in figure 3, t is the thickness of the web plate, A_a and A_b are the areas of

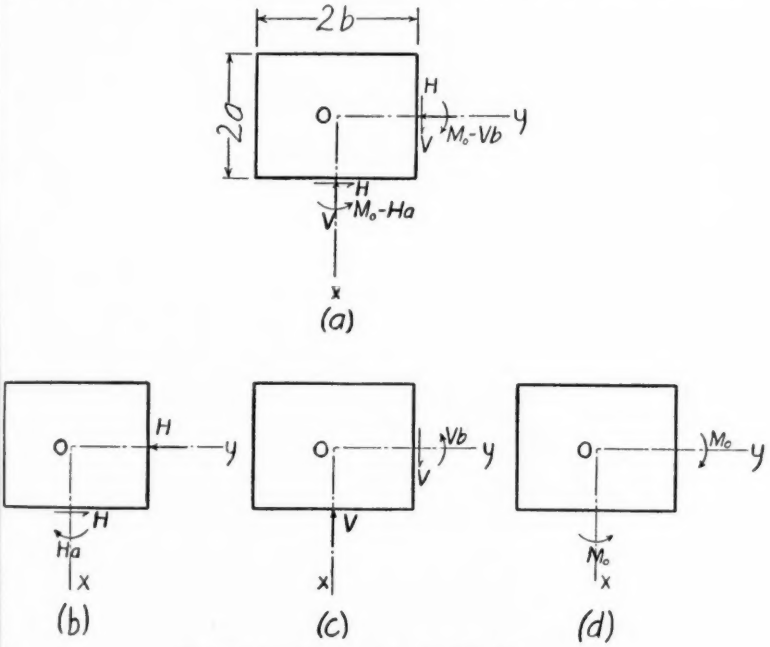

FIGURE 3.—*Loads on knee of rigid frame.*

cross sections parallel to the axes of x and y, respectively, and I_a and I_b are the least moments of inertia of A_a and A_b, respectively, with respect to axes perpendicular to the web plate.

For the case of figure 3 (b)

$$\left.\begin{aligned}
\sigma_x &= \frac{Hay}{I_b}\left[\frac{1}{2}\left(1+\frac{x}{a}\right)-\frac{at}{2A_a}\left(1-\frac{x^2}{a^2}\right)+\frac{b^2t}{3aA_a}\left(1-\frac{4b^3t}{15I_b}-\frac{y^2}{b^2}\right)\right],\\
\sigma_y &= -\frac{H}{2A_a}\left(1+\frac{y}{b}\right)\left[1+\frac{b^3t}{3I_b}\frac{y}{b}\left(1-\frac{y}{b}\right)\right],\\
\tau_{xy} &= \frac{Hab^2t}{2A_aI_b}\left(\frac{A_a}{2at}+\frac{x}{a}\right)\left(\frac{1}{3}+\frac{I_b}{b^3t}-\frac{y^2}{b^2}\right).
\end{aligned}\right\} \quad (1)$$

This solution satisfies the following boundary conditions:

$$y=-b\colon\ \sigma_y=0;$$
$$x=-a\colon\ \int_{A_b}\sigma_x dA=0;$$
$$x=-a\colon\ \int_{A_b}\sigma_x y dA=0.$$

The solution for the case of figure 3 (c) is obtained from the preceding solution by replacing H by V and interchanging a and b and x and y:

$$\left.\begin{aligned}
\sigma_x&=-\frac{V}{2A_b}\left(1+\frac{x}{a}\right)\left[1+\frac{a^3t}{3I_a}\frac{x}{a}\left(1-\frac{x}{a}\right)\right],\\
\sigma_y&=\frac{Vbx}{I_a}\left[\frac{1}{2}\left(1+\frac{y}{b}\right)-\frac{bt}{2A_b}\left(1-\frac{y^2}{b^2}\right)+\frac{a^2t}{3bA_b}\left(1-\frac{4a^3t}{15I_a}-\frac{x^2}{a^2}\right)\right],\\
\tau_{xy}&=\frac{Va^2bt}{2A_bI_a}\left(\frac{A_b}{2bt}+\frac{y}{b}\right)\left(\frac{1}{3}+\frac{I_a}{a^3t}-\frac{x^2}{a^2}\right).
\end{aligned}\right\}\quad(2)$$

The following boundary conditions are satisfied:

$$x=-a\colon\ \sigma_x=0;$$
$$y=-b\colon\ \int_{A_b}\sigma_y dA=0;$$
$$y=-b\colon\ \int_{A_a}\sigma_y x dA=0.$$

For the case of figure 3(d)

$$\left.\begin{aligned}
\sigma_x&=-\frac{M_0y}{I_b}\left[\frac{1}{2}\left(1+\frac{x}{a}\right)\left[1+\frac{1}{3}\frac{a^3t}{I_a}\frac{x}{a}\left(1-\frac{x}{a}\right)\right]\right.\\
&\quad\left.-\frac{a^5b^2t}{3(a^4+b^4)I_a}\frac{x}{a}\left(1-\frac{4b^3t}{15I_b}-\frac{y^2}{b^2}\right)\right],\\
\sigma_y&=-\frac{M_0x}{I_a}\left[\frac{1}{2}\left(1+\frac{y}{b}\right)\left[1+\frac{1}{3}\frac{b^3t}{I_b}\frac{y}{b}\left(1-\frac{y}{b}\right)\right]\right.\\
&\quad\left.-\frac{a^2b^5t}{3(a^4+b^4)I_b}\frac{y}{b}\left(1-\frac{4a^3t}{15I_a}-\frac{x^2}{a^2}\right)\right],\\
\tau_{xy}&=-\frac{M_0a^2b^2t}{4I_aI_b}\left[\left(\frac{1}{3}+\frac{I_a}{a^3t}-\frac{x^2}{a^2}\right)\left(\frac{1}{3}+\frac{I_b}{b^3t}-\frac{y^2}{b^2}\right)\right.\\
&\quad-\frac{a^2b^2}{3(a^4+b^4)}\left[\left(1-\frac{x^2}{a^2}\right)^2-\frac{8a^3t}{15I_a}\left(\frac{1}{3}+\frac{I_a}{a^3t}-\frac{x^2}{a^2}\right)\right.\\
&\quad\left.\left.+\left(1-\frac{y^2}{b^2}\right)^2-\frac{8b^3t}{15I_b}\left(\frac{1}{3}+\frac{I_b}{b^3t}-\frac{y^2}{b^2}\right)\right]\right].
\end{aligned}\right\}\quad(3)$$

This solution satisfies the following boundary conditions:

$$x=-a\colon\ \int_{A_b}\sigma_x dA=0;$$
$$x=-a\colon\ \int_{A_b}\sigma_x y dA=0;$$
$$y=-b\colon\ \int_{A_a}\sigma_y dA=0;$$
$$y=-b\colon\ \int_{A_a}\sigma_y x dA=0.$$

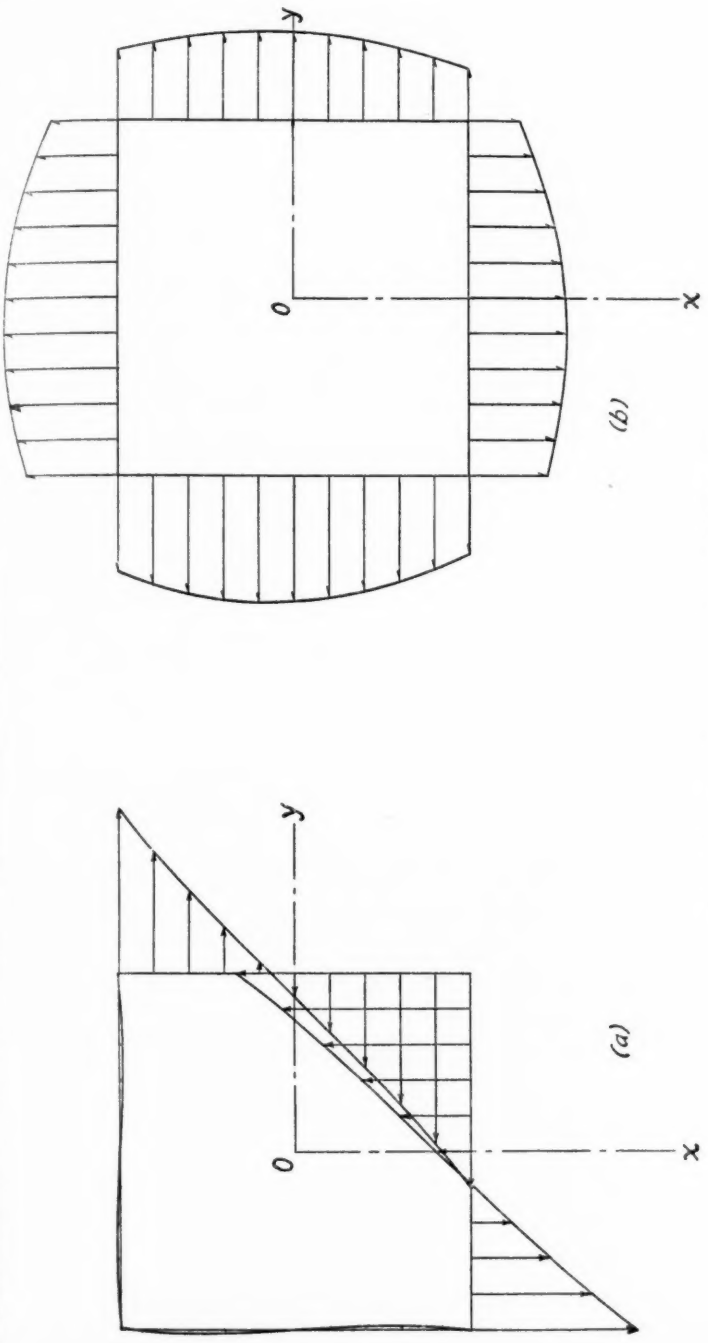

FIGURE 4.— *Boundary stresses, knee of rigid frame.*

Example.—In order to illustrate the distribution of stress given by the preceding analysis, consider the knee of a rigid frame for which[2]

$$a=b=18.65 \text{ in.}$$
$$t=3/8 \text{ in.}$$
$$A_a=A_b=32.44 \text{ sq. in.}$$
$$I_a=I_b=8{,}102 \text{ in.}^4$$
$$H=43{,}310 \text{ lb.}$$
$$V=61{,}230 \text{ lb.}$$
$$M_0=5{,}725{,}000 \text{ lb in.}$$

Figure 4 (a) shows the distribution of normal stresses on the four sides of the knee, and figure 4 (b) shows the distribution of shearing stresses in the web plate of the knee along the centroids of the flanges. It may be noted that the normal stresses along the edges $x=-a$ and $y=-b$ are small. The maximum value does not exceed 180 lb per sq in., whereas the maximum normal stress, $-\sigma_x$, at $x=a$, $y=b$ is 13,270 lb per sq in. (compression).

If there are no flanges present, then $A_a=2at$, $A_b=2bt$, $I_a=(2/3)a^3t$, $I_b=(2/3)b^3t$, and solutions 1 and 2 for the cases of figures 3 (b) and (c) reduce to the well-known solution for a uniformly loaded cantilever beam.[3] Solution 3 for the case of figure 3 (d) reduces to

$$\sigma_x=-\frac{3M_0y}{2b^3t}\left[\frac{1}{2}\left(1+\frac{x}{a}\right)^2\left(1-\frac{x}{2a}\right)-\frac{a^2b^2}{2(a^4+b^4)}\,\frac{x}{a}\left(\frac{3}{5}-\frac{y^2}{b^2}\right)\right],$$

$$\sigma_y=-\frac{3M_0x}{2a^3t}\left[\frac{1}{2}\left(1+\frac{y}{b}\right)^2\left(1-\frac{y}{2b}\right)-\frac{a^2b^2}{2(a^4+b^4)}\,\frac{y}{b}\left(\frac{3}{5}-\frac{x^2}{a^2}\right)\right],$$

$$\tau_{xy}=-\frac{9M_0}{16abt}\left\{\left(1-\frac{x^2}{a^2}\right)\left(1-\frac{y^2}{b^2}\right)\right.$$
$$\left.-\frac{a^2b^2}{3(a^4+b^4)}\left[\left(1-\frac{x^2}{a^2}\right)\left(\frac{1}{5}-\frac{x^2}{a^2}\right)+\left(1-\frac{y^2}{b^2}\right)\left(\frac{1}{5}-\frac{y^2}{b^2}\right)\right]\right\}.$$

If the second of each of the two terms on the right-hand sides of these expressions is omitted, the approximate solution given by Föppl[4] is obtained. The second terms are necessary to satisfy the conditions of compatibility.

WASHINGTON, September 11, 1941.

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U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1432

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ESTIMATION OF ALDEHYDE GROUPS IN HYDROCELLULOSE FROM COTTON

By Albert R. Martin,[1] Leonard Smith,[1] Roy L. Whistler,[1] and Milton Harris [1]

ABSTRACT

The aldehyde content of hydrocellulose may be readily estimated by titration with iodine in alkaline solution. Investigation of the rate of oxidation of hydrocellulose by iodine at 0° C and pH 10.6 showed that there is an initial rapid reaction in the first hour accompanied by a side reaction. This latter reaction continues after the rapid reaction has ceased and consumes iodine slowly at a constant rate. Purified cotton cellulose shows an initial reaction with iodine and after 1 hour exhibits a side reaction of the same rate as the hydrocellulose. By applying a correction for the amount of iodine consumed in the side reaction, it is possible to estimate the iodine utilized in the oxidation of aldehyde groups. Since iodine utilized in this way converts aldehyde to carboxyl groups, an independent check on the value obtained with iodine is readily obtained by estimation of the carboxyl groups thus formed by titration with silver *o*-nitrophenolate. It is shown that the extent of hydrolytic degradation as determined by this method compared well with similar measurements by the viscosity method.

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I. INTRODUCTION

A number of methods have been proposed at various times for the estimation of the aldehyde content of degraded cellulosic materials. Probably the most widely used among these has been the copper number method. The disadvantages of most of the methods have frequently been discussed and reviewed in the literature [1, 2, 3, 4, 5] [2] and need not be further considered here.

[1] Research Associates at the National Bureau of Standards, representing the Textile Foundation.
[2] Figures in brackets indicate literature references at the end of this paper.

The method of Bergmann and Machemer [6], which involves the use of iodine in alkaline solution, seemed to offer considerable promise even though it has been rather severely criticized by a number of workers [7, 8, 9]. This method is based on the ability of iodine in alkaline solution to oxidize aldehyde groups to carboxyl groups [23], and is used in somewhat the same manner as earlier methods for the oxidation of glucose and other aldehyde sugars [10, 11]. It has been shown that aldoses are quantitatively oxidized to the corresponding aldonic acids by iodine in alkaline solution [10, 23].

The claims of Bergmann and Machemer that the iodine consumed by cellulose is selectively confined to the oxidation of free aldehyde groups to carboxyl groups and that the reaction is of a stoichiometric nature have been disputed, especially by Hess and his coworkers [7], Brissaud [8], and Sakurada [9]. The principal criticisms have been that the consumption of iodine does not cease at any given time but proceeds more or less indefinitely, and accordingly that the reaction is not stoichiometric.

In the present investigation, a study was made of the factors which influence the consumption of iodine by glucose and by cotton cellulose. Preliminary experiments indicated that the above-mentioned criticisms were valid and that the results were erratic when the procedure described by Bergmann and Machemer was followed. The values obtained for the content of reducing groups in a given sample of degraded cellulose depended on a number of conditions; for example, the length of time the reaction was allowed to proceed, the temperature, and the pH values of the iodine solutions. The experiments further indicated that more than one reaction was taking place. This, however, was not surprising since in practically all methods which have been devised for the estimation of reactive or functional chemical groups in natural products, such as the proteins or cellulosic materials, this same difficulty has been encountered. An explanation for such behavior is found in the fact that these materials are extremely complex and contain so many reactive groups that the elimination of side reactions is practically impossible.

It is shown in the present paper, that the extent of the side reaction can be determined and accordingly a correction can be made for the amount of iodine consumed in this way. The remainder of the iodine is used to oxidize aldehyde groups to carboxyl groups, as shown by direct estimation of the carboxyl groups thus formed.

II. EXPERIMENTAL PROCEDURE

1. MATERIALS

Raw cotton was dewaxed by extraction with hot alcohol for 24 hours and then washed thoroughly with cold distilled water. The cotton was further purified by boiling with a 1-percent solution of sodium hydroxide for 8 hours. The procedure was essentially the same as that described by Corey and Gray [12] except that the apparatus of Worner and Mease [13] was used.

A series of hydrocelluloses of different fluidities were prepared by steeping samples of the purified cotton in hydrochloric acid solutions, ranging in concentrations from 0.5 to 5.0 *N*, for 24 hours. The temperature of the solutions was 21°C. The samples were finally washed with distilled water until the wash waters were neutral to litmus.

2. ANALYTICAL METHODS

The fluidities of dispersions of purified cellulose and of the hydrocelluloses in cuprammonium hydroxide reagent were determined by the method of Clibbons and Geake [14], as modified by Mease [15]. Carboxyl contents were determined by measuring the amount of silver bound by the fiber from a solution of silver *o*-nitrophenolate, according to the procedure described by Sookne and Harris [16].

3. DESCRIPTION OF THE IODINE TITRATION

The amount of iodine consumed by the materials used in this work was determined as follows: 100 ml of a buffer solution at approximately pH 10.6, prepared by mixing 15 parts of 0.2*M* sodium carbonate and 1 part of 0.2*M* sodium bicarbonate, was pipetted into a 500-ml glass-stoppered Erlenmeyer flask and then cooled to 0° C in a thermostat. 25 ml of a 0.0500 *N* iodine solution coutaining 40 g of potassium iodide per liter, previously cooled to 0° C, was then added and the sample to be titrated immediately introduced. In the experiments with glucose, 0.05 g of the sugar was used; with cotton, about 1-g samples were used. At the end of a specified time interval, 10 ml of 5 *N* HCl was added and the iodine remaining in the solution was measured by titration with standard sodium thiosulfate to the starch end point.

When analyses were made on cotton, the mixture was swirled during addition of thiosulfate. Near the end point the solution became very nearly colorless although the sample still contained some iodine, as indicated by the brown color of the fiber. At this point, addition of the thiosulfate was stopped, the stopper replaced in the flask, and the mixture vigorously shaken. Care was taken to release the stopper of the flask frequently during this operation, since carbon dioxide was released from the solution. After the mixture was shaken, the titration was completed to the point where both the solution and sample were colorless.

Blank determinations on identical solutions which did not contain either glucose or cotton were made for each time period. This is necessary since it has been shown [17] that the recovery of iodine from alkaline solution is not quantitative. From the difference in amount of thiosulfate required by the blank solution and by the solution containing the sample, the number of milliequivalents of iodine consumed per gram of dry sample was calculated.

III. RESULTS AND DISCUSSION

1. EFFECT OF TEMPERATURE AND pH ON THE RATE OF OXIDATION OF GLUCOSE BY IODINE

In order to obtain information on the effect of temperature and pH on the rate of oxidation of aldehyde groups with iodine, a few preliminary experiments were made with glucose. While it is recognized that the conditions which are optimum for the oxidation of aldehyde groups in soluble sugars may not necessarily be optimum for similar oxidation of aldehyde groups in cellulosic materials, the assumption was made that they are probably not greatly different.

The results at two temperatures, 0° and 25° C, and at several pH values are shown in figure 1. From the curves it is seen that the rate of oxidation increases rapidly with increase in temperature and pH. Whereas equilibrium was not reached even in 6 hours at pH 9.2 and 0° C, it was reached in slightly over an hour at pH 9.2 and 25° C or at pH 10.6 and 0° C.

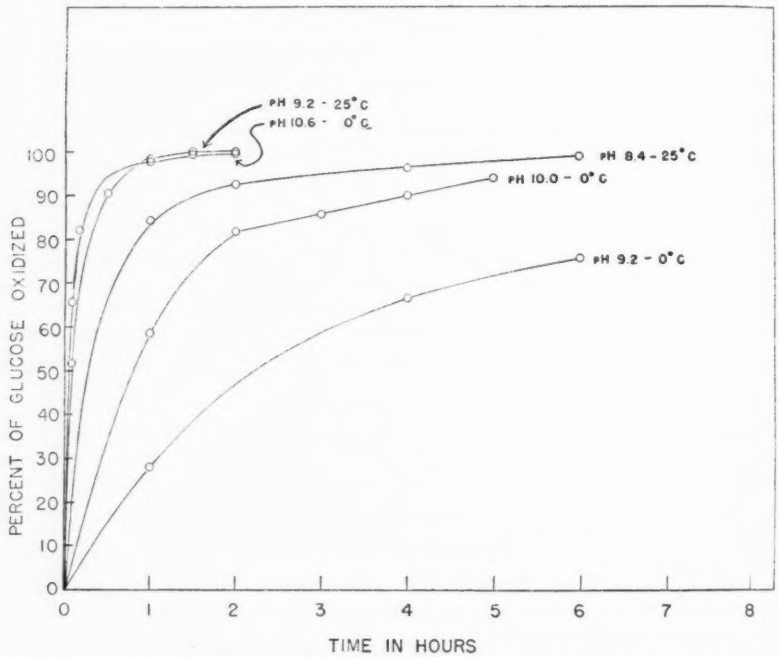

FIGURE 1.—*Effect of* pH *and temperature on the rate of oxidation of glucose in iodine solutions.*

2. APPLICATION OF THE METHOD TO COTTON CELLULOSE

From the foregoing, it appeared that either of the latter two sets of conditions, namely pH 9.2 and 25° C or pH 10.6 and 0° C, could be used for experiments with cotton. A few preliminary tests, however, indicated that with cotton the rate of the side reaction was appreciably increased at the higher temperature. For this reason all further experiments were conducted at 0° C and pH 10.6.

When samples of purified cotton and a hydrocellulose (27.8 rhes) were titrated with the iodine solution, the results shown in figure 2 were obtained. In both cases there was an initial rapid consumption of iodine during the first hour of treatment, after which iodine was consumed at a much lower but approximately constant rate. By analogy with glucose, it appears that the initial rapid reaction of the cellulose with iodine involves the oxidation of aldehyde groups to carboxyl groups. The reaction does not reach a definite end point,

however, and the slower side reaction (straight-line portions of the curves) involves the consumption of iodine presumably in some other way. Support is lent to this idea by the fact that the straight-line portions of both curves are closely parallel and that the only difference then is the extent of the primary reaction, which would be expected to be greater for the hydrocellulose. The difference between the parallel curves would then be a measure of the aldehyde groups formed in the hydrolytic degradation of the purified cotton.

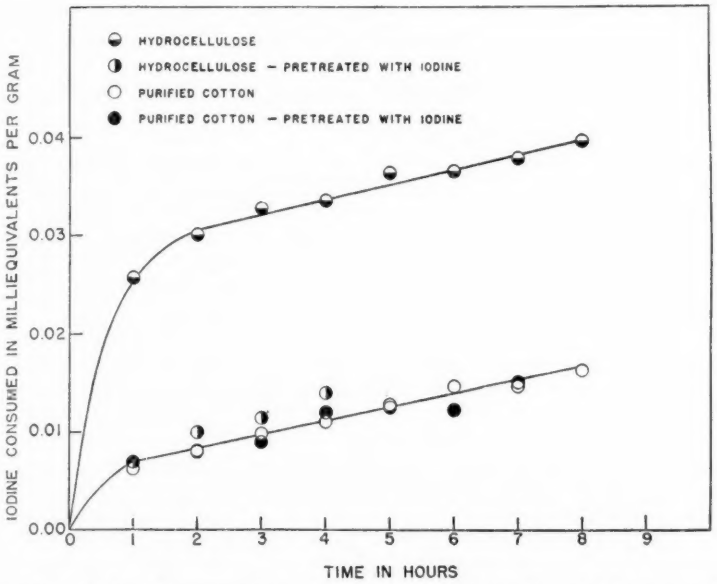

FIGURE 2.—*Rates of consumption of iodine by purified cotton and by a sample of hydrocellulose (27.8 rhes) from solutions at* pH *10.6 and 0° C.*

Attention is now directed to the curve for the purified cotton. It would appear from the rapid initial consumption of iodine that there was an appreciable number of reducing groups in the purified cotton. Indeed, this was assumed to be the case until measurements were made of the carboxyl contents of the samples which had been oxidized with iodine. When this was done (as shown in the following section), no increase in the carboxyl content comparable to the initial increase in iodine consumed was noted. This immediately led to the conclusion that the amount of iodine initially taken up by the purified cotton was not utilized in oxidation of aldehyde to carboxyl groups but was used up in some unidentified manner. Further evidence supporting this view was obtained from the following experiments. Samples of the purified cotton and the hydrocellulose were pretreated with iodine for 2 hours by the method previously described except that the reaction mixture was not acidified. Instead, the samples were thoroughly washed with distilled water until the wash waters showed no reaction with litmus or to starch solution. Samples of these materials were

then subjected to the regular iodine titration, the results being shown in figure 2. Pretreatment of the purified cotton did not significantly alter the amount of iodine consumed. On the other hand, the pretreated hydrocellulose consumed iodine at very nearly the same rate as the purified cotton, indicating that the aldehyde groups of the hydrocellulose had been oxidized during the pretreatment. From these results, it appears that the purified cotton does not contain a measurable number of aldehyde groups. However, the possibility that aldehyde groups may have been in the cellulose before purification of the fiber cannot be overlooked, although some arguments against this possibility have already been presented elsewhere [18, 19, 20].

On the basis of the foregoing, it is seen that the content of aldehydic reducing groups in the hydrocellulose is obtained from the difference between the straight-line portions of the curves in figure 2. The average of the differences, obtained by subtracting the amount of iodine consumed by the purified cotton from that consumed by the hydrocellulose for each time interval between 2 and 8 hours, is 0.023 milliequivalent of iodine per gram. Since 2 equivalents of iodine are required to oxidize each aldehyde group to a carboxyl group, it follows that the content of aldehydic reducing groups of the hydrocellulose is one-half of this value, or 0.0115 millimole per gram.

In using this method for the examination of an "unknown" sample of hydrocellulose, it is necessary to have available a blank determination on undegraded cellulose of the same kind. If it appears that the sample was obtained from cotton, then the blank determination can be made on a sample of raw cotton purified by the ACS method, or the curve for purified cotton as given in this paper could be used.

A method of more general applicability is the "pretreatment" method described above. By this method, the first treatment with iodine gives a result corresponding to the aldehyde groups plus the blank. A second treatment of the same sample gives a result corresponding to the blank only.

3. ESTIMATION OF THE CARBOXYL GROUPS IN THE CELLULOSE AFTER OXIDATION WITH IODINE

It has been assumed in the foregoing section that the iodine consumed in the primary reaction is utilized in the oxidation of aldehyde to carboxyl groups. As a check on this assumption, the carboxyl contents of the purified cotton and hydrocellulose, after oxidation with iodine, were determined by titration with silver *o*-nitrophenolate [16]. In these experiments, the samples were first treated with iodine solutions for varying periods of time, as previously described, except that the solutions were not acidified, the iodine being carefully washed from the fiber with distilled water. The results are shown in figure 3.

As seen from the lower curve, the carboxyl content of the purified cotton increased slowly and at an approximately constant rate. As pointed out previously, there is no initial rapid rise in the curve equivalent to that found in the iodine-titration curve for the same material (fig. 2).

On the other hand, the amount of silver bound by the oxidized hydrocellulose is considerably higher. Treatment of the hydrocellulose with iodine for periods longer than 2 hours resulted in still higher

silver-binding capacities. However, the increase is at the same rate as that found for the purified cotton. Apparently, the iodine consumed in the side reaction is utilized in oxidizing groups other than the aldehyde groups inititally in the cellulose, although the nature of this oxidation is not known at this time.

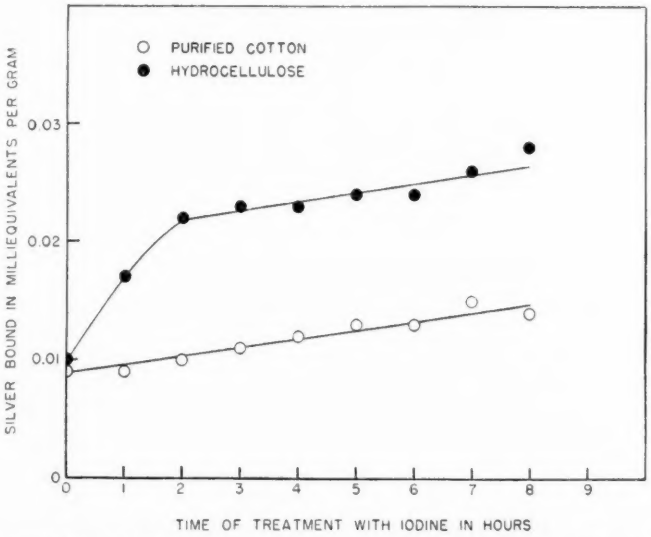

FIGURE 3.—*Silver-binding capacities of samples of purified cotton and of a hydrocellulose (27.8 rhes) after treatment with iodine for different lengths of time.*

The average difference between the straight-line portions of the curves is 0.012 milliequivalent of silver per gram, indicating that an equivalent number of carboyxl groups were formed during the primary reaction of the iodine with cellulose. This value is in excellent agreement with the estimated content of aldehyde groups (0.0115 millimole per gram) determined directly by the iodine-titration method.

4. APPLICATION OF THE METHOD TO A SERIES OF HYDROCELLULOSES

Since the straight-line portions of the curves in figure 2 are so closely parallel, the content of aldehyde groups can be readily estimated from the difference between the curves at any time interval greater than 2 hours. In the subsequent experiments, the amount of iodine consumed by a series of hydrocelluloses in 3 hours was compared with that consumed by the purified cotton during the same time. A second set of the same series was similarly treated with iodine and then titrated with silver *o*-nitrophenolate, as already described. The data are given in table 1.

TABLE 1.—*Aldehyde contents of a series of hydrocelluloses*

Fluidity of hydrocellulose	Aldehyde content	
	From titration with iodine	From silver-binding capacity after oxidation with iodine
Rhes	*Millimole/g*	*Millimole/g*
• 1.2	0.000	0.000
3.2	.002	.002
5.2	.002	.003
10.0	.003	.003
15.3	.005	.005
21.9	.007	.009
26.9	.011	
27.8	.012	.012

• Purified cotton.

5. ESTIMATION OF MOLECULAR WEIGHTS

In the hydrolytic degradation of cellulose, an aldehyde group is produced at each point ruptured—that is, each hydrocellulose molecule formed as a result of splitting the original cellulose molecule contains an aldehyde end-group. The molecular weight[3] (number-average) of the system at any stage of degradation may therefore be obtained from the following equation:

$$M=\frac{W}{n+\alpha}, \tag{1}$$

where M=the molecular weight,
W=the weight of cellulose,
n=the number of moles of cellulose originally present, and
α=the number of moles of hydrocellulose formed during the hydrolysis=the number of aldehyde groups.

α is readily estimated by the iodine-titration method, but since the cellulose molecules in the purified cotton apparently do not contain free aldehyde groups, n cannot be determined in this way. Accordingly, the molecular weights cannot be directly estimated from iodine-titration data except in the special case where the degree of degradation is very high. In such a system n becomes very small compared with α, and a good approximation of M is obtained directly from W/α.

If n is determined independently, then the molecular weight of the system at any stage of degradation is determined by eq 1. Thus the molecular weights of the series of hydrocelluloses referred to in the previous section have been calculated, using a value of n obtained from fluidity measurements of purified cotton. These are shown in table 2 and compared with molecular weights obtained by the fluidity method. Since the iodine method gives a number-average[4] molecular weight and the fluidity method, a weight-average[4] molecular weight, it must be emphasized that the agreement in absolute values is entirely fortuitous [21, 22, 24]. An important feature of the data, however, is that they indicate good agreement between the extents

[3] The term "molecular weight" is used here with the same meaning that has been given it by Staudinger [25] and by Kraemer [26].
[4] The terms "number-average" and "weight-average" used here have been defined by Lansing and Kraemer [24].

of hydrolytic degradation as measured by the fluidity and iodine-titration methods.

TABLE 2.—*Comparison of molecular weights calculated from fluidity measurements and by the iodine-titration method*

Fluidity	Aldehyde content	Molecular weight from fluidity	Molecular weight from iodine method [b]
Rhes	*Millimole/g*		
[a]1.22	0.000	307,000	----------
3.24	.002	224,000	189,000
5.19	.002	187,000	189,000
10.02	.003	133,000	160,000
15.3	.005	99,000	121,000
21.9	.007	73,000	97,000
26.9	.011	60,000	70,000
27.8	.012	58,000	65,000

a Purified cotton.
b Calculated using eq 1 in the text. The value of n in the equation was obtained from fluidity measurements of the purified cotton.

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NATURE OF THE RESISTANCE OF WOOL TO DIGESTION BY ENZYMES

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ABSTRACT

Wool that has neither been injured mechanically nor modified chemically is completely resistant to attack by the proteolytic enzymes—pepsin, trypsin, chymotrypsin, and papain. When the cuticle or scale layer of the fibers is damaged by mechanical means, the wool becomes susceptible to attack by pepsin and chymotrypsin. Under these conditions only a small portion of the wool is digested, yet the fibers are considerably weakened and their fibrous structure is partly destroyed.

Wool in which the disulfide cross-linkages have been broken, as by reduction, or by reduction followed by methylation, is almost completely digested by pepsin and chymotrypsin, but is attacked only slightly by trypsin. When the reduced wool is reoxidized and its sulfhydryl groups are converted to disulfide groups, the wool regains its original stability. When the sulfhydryl groups of the reduced wool are converted to *bis*-thioether groups by the action of an aliphatic dihalide, the stability of the wool toward enzymes is greatly enhanced.

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I. INTRODUCTION

Proteins of the class called keratins, of which wool is a member, are so characteristically resistant to digestion by enzymes, that this phenomenon is usually included in the definition of the keratin group [1].[2] The exact reason for this resistance has not been entirely clear,

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[2] Figures in brackets indicate the literature references at the end of this paper.

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but on the basis of earlier work on wool it seems due to a stability resulting from the presence of disulfide cross-linkages between the polypeptide chains of the protein [2, 3], or to a resistance to diffusion of the enzyme into the fibers, brought about by an impermeable outer layer of scales or by the walls of the cells composing the fiber. For example, wool previously treated with alkali has been reported by Meunier, Chambard, and Comte [4], and by Fromageot and Porcherel [5] to be disintegrated into spindle-shaped cells by the action of preparations of pancreatic proteinases. Products resulting from the oxidation of human hair by solutions of bromine in glacial acetic acid, or by solutions of hydrogen peroxide in 0.4 *N* sulfuric acid, have been described by Stary and by Waldschmidt-Leitz and Schuckmann [6] as digestible by trypsin. An enzyme discovered by Linderstrøm-Lang and Duspiva [7] in the intestinal tract of the clothes moth was found capable of digesting wool in an alkaline and strongly reducing environment. Goddard and Michaelis [8] found that the amorphous reduction products obtained from wool by the action of alkaline thioglycolate solutions, or of other alkaline reducing agents, were digested by pepsin or trypsin. More recently, Routh and Lewis [9, 10] observed that wool powdered by prolonged grinding in a ball mill was changed chemically as well as physically, with the result that it became partly digestible.

Although all of the above-mentioned treatments affect the disulfide groups, none of them can be considered to involve these groups alone, so it cannot be finally concluded, on the basis of the earlier work, that the disulfide cross-linkages are responsible for the resistance of wool protein to digestion by enzymes; nor can the influence of histological structure be evaluated, since those treatments which destroy the fiber structure—such as grinding in a ball mill or reduction in strongly alkaline thioglycolate solution—produce other far-reaching changes as well.

There are still other barriers to drawing exact conclusions from the earlier studies. The preparations of enzymes used have usually not been pure crystalline substances, but have consisted of crude concentrates [4, 5, 8, 11]. Moreover, the methods available for detecting attack by enzymes have not been very sensitive, since they have depended on measurement of loss in weight [4], of determination of material not precipitable by sulfosalicylic acid [8], or merely of microscopic observation of the extent of disintegration [11]. Such methods are satisfactory when a considerable portion of the protein is digested, but are inadequate when the extent of digestion is small.

In the present investigation it was possible to overcome most of these objections. Chemical reactions that rupture disulfide bonds and minimize the possibility of secondary chemical reactions have recently been developed in this laboratory [3]. The development of methods for preparing crystalline enzymes by Northrop [11] and by Balls and Lineweaver [12] has made possible the use of preparations of enzymes of known identity and purity. Finally, it was possible to follow the attack of enzymes on the wool protein by noting changes in the mechanical properties of the fiber.

II. EXPERIMENTAL PROCEDURE

1. MATERIALS

The wool fibers used in the present study were a portion of the lot used in previous investigations in this laboratory [3, 13]. This wool had been subjected to no chemical or mechanical treatment other than successive extraction with alcohol and with ether, followed by washing with water at 40° C.

Crystalline pepsin, trypsin, chymotrypsin, and papain [3] were used in this work. The papain preparation consisted of a suspension of the crystalline enzyme in a 0.02 *M* solution of sodium cyanide.

The solutions of pepsin with which the fibers were treated contained 1 mg of crystalline enzyme per milliliter of a solution of 0.1 *M* potassium chloride, and were adjusted to a pH value of 1.5 by the addition of hydrochloric acid. The solutions of crystalline trypsin and chymotrypsin each contained 1 mg of the crystalline enzyme per milliliter of a 0.1 *M* solution of potassium phosphate at a pH value of 7.0. The solutions of crystalline papain were prepared from the suspension described above, by diluting it with water to a concentration of 0.16 mg of protein nitrogen per milliliter and adjusting to pH 7.0 by the addition of dilute acetic acid. The addition of small amounts of merthiolate effectively prevented the growth of bacteria in all of these solutions.

A commercial trypsin[4] was also used in some experiments. In these experiments, 10 mg of enzyme preparation per milliliter of 0.05 *M* potassium phosphate at pH 7.0 was used. The solutions of commercial trypsin were kept sterile by the addition of small amounts of thymol.

2. METHODS

a. DETECTION OF ATTACK BY ENZYMES

The attack by the enzymes was followed by measuring the stress-strain characteristics of the fibers at different stages of treatment. This method has the advantage that it can detect amounts of digestion too small to be detectable by the usual methods. It[5] depends upon the fact that a wool fiber that has been immersed in water or a neutral buffer solution and stretched under load until it is elongated 30 percent will return almost to its original length when the load is removed. If the fiber is allowed to relax in the unstretched state in water or in the neutral buffer solution for about 24 hours and then again stretched until elongated 30 percent, it is found that the same amount of energy (within about 1 percent) is required for the second stretching as for the first. However, if some treatment that weakens the fiber is interposed between the two stretchings, it is found that a lesser amount of energy is required the second time. In such a case, the ratio of the energy required for the second stretching to that required for the first is known as the *30-percent index* of the fiber. A fiber that has been stretched the first time is hereafter referred to as a *calibrated fiber*.

[3] Acknowledgment is made to J. H. Northrop, of the Rockefeller Institute for Medical Research, for a gift of crystalline trypsin and chymotrypsin, and to A. K. Balls, of the U. S. Department of Agriculture, for a gift of crystalline chymotrypsin and papain.

[4] The term "commercial trypsin" is used in this paper to indicate a relatively crude preparation of enzyme material prepared from pancreatic juice and available from commercial sources.

[5] The mechanical details are presented elsewhere [13].

All stress-strain measurements were made on fibers in 0.2 *M* phosphate buffer solution at pH 7.0. Calibrated fibers that had been treated with solutions of enzymes were always washed thoroughly with distilled water, and then kept in the phosphate buffer solution at pH 7.0 for at least 20 hours before stretching them a second time.

b. CHEMICAL TREATMENTS

Methods for the preparation of derivatives of wool in which the disulfide cross-linkages have been ruptured without visibly affecting the fiber structure have previously been described in detail [3]. The methods involve reducing the wool with thioglycolic acid solutions followed by treating the reduced product with an alkyl halide. The reactions appear to involve only the disulfide groups of the cystine in wool, and may be represented by the following equations:

$$W-S-S-W+2HS-CH_2-COOH\longrightarrow 2W-SH+(HOOC-CH_2-S)_2 \quad (1)$$

$$W-SH+RX\longrightarrow W-SR+HX \quad (2)$$

$$W-SH+CH_2X_2\longrightarrow W-S-CH_2-S-W+2HX, \quad (3)$$

where W represents the portions of the wool molecule connected by the disulfide groups, R an alkyl group, and X a halogen atom.

The reduced and the reduced and alkylated wool fibers used in the present investigation contained between 4 and 6 percent of unchanged cystine. The cystine content of the untreated wool was 12.4 percent. The reduced and reoxidized wool fibers were prepared by reducing wool to about this same cystine content, and reoxidizing with oxygen as previously described [3].

c. MECHANICAL TREATMENTS

The mechanically "injured" fibers were prepared by placing calibrated fibers on a glass plate, and tapping them at about six places along their length with a rounded glass rod. Such fibers, on examination under the microscope, appeared to be injured, since crevices were formed and cuticle scales lost in the tapped regions. At this point in the procedure, the mechanically injured fibers were again calibrated, and those that had 30-percent indices less than 0.96 were discarded.

d. ENZYME TREATMENTS

Each fiber, after the calibration and the subjection to either mechanical or to chemical treatments, was placed in a small test tube. One milliliter of the solution of enzyme was added and permitted to act for the specified period at 20° to 25° C. In order to be sure that the effects observed were the results of the action of enzymes, control experiments were always carried out, in which another group of calibrated fibers was exposed to the action of identical solutions, except that no enzyme was present.

III. RESULTS AND DISCUSSION

The results of the action of the different enzymes upon wool fibers are summarized in the following sections.

FIGURE 3.—*Cross sections of wool fibers treated with pepsin.* ×450.

A, Sections of untreated fibers treated with pepsin for 30 days; *B*, sections of reduced and methylated fibers treated with pepsin for 10 days; *C*, sections of reduced and methylated fibers treated with pepsin for 30 days.

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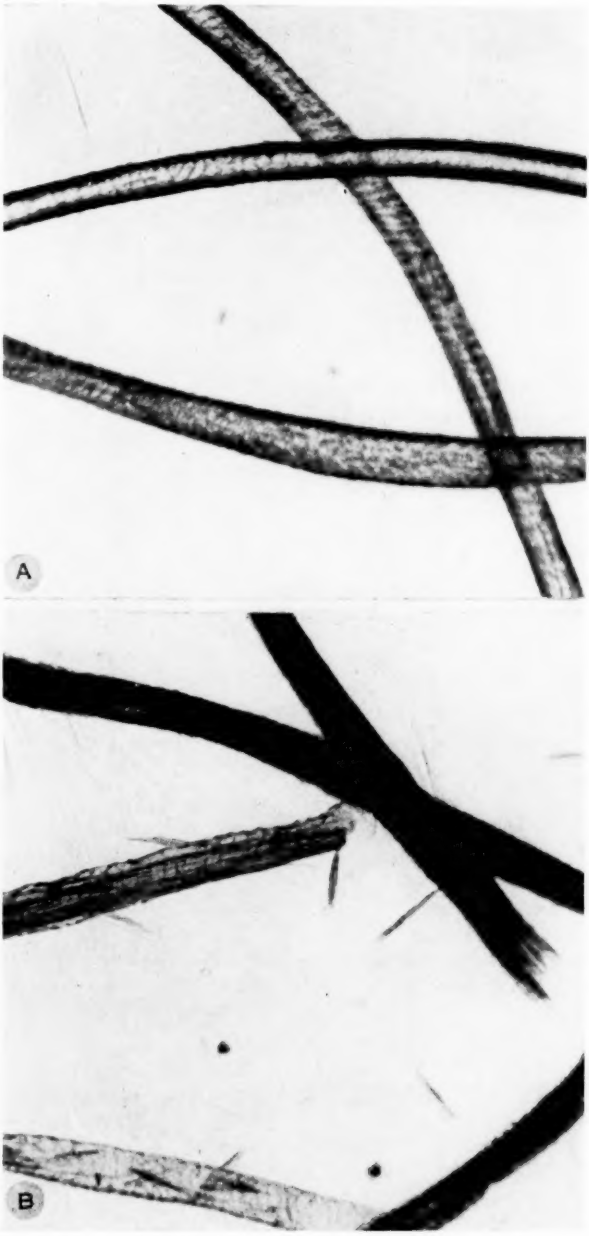

FIGURE 2.—*Untreated wool fibers (A) and reduced and methylated wool fibers (B) after treatment with pepsin.* ×150.

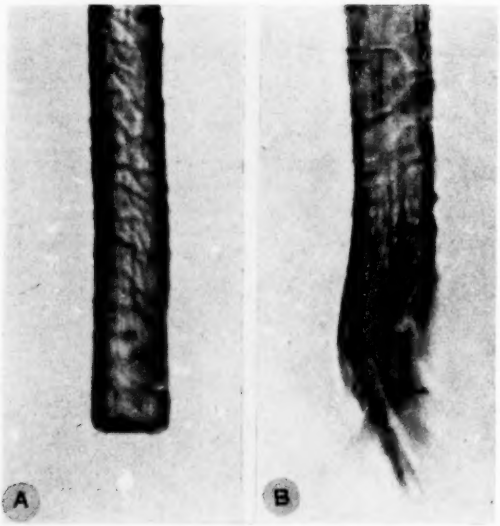

FIGURE 1.—*Broken ends of untreated wool fibers (A) and mechanically damaged woo fibers (B) after treatment with pepsin.* ×250.

1. CRYSTALLINE PEPSIN

During periods up to 10 days, solutions of crystalline pepsin had no appreciable effect upon the untreated fibers, as indicated by the fact that the 30-percent indices remained high, averaging 0.96 (table 1). When the treatment was prolonged to 30 days, the fibers disintegrated at the slightest touch. However, fibers in a similar but enzyme-free solution adjusted to a pH value of 1.5 were found to be considerably weakened, the 30-percent index falling to 0.77; and such fibers, when transferred to pepsin solution, were almost immediately attacked by the enzyme. It is thus seen that undamaged fibers are not attacked by pepsin, but that solutions acid enough for the optimum activity of pepsin gradually attack the fibers and make them susceptible to the action of the enzyme.

Crystalline pepsin readily attacked mechanically damaged fibers, and weakened them so that they broke at 5- to 10-percent elongation. The broken ends of the mechanically damaged, pepsin-treated fibers showed ragged breaks, at which clearly outlined cortical cells were visible, and not the sharp, straight break characteristic of untreated fibers, as may be seen by comparison of figure 1 (*A*) with figure 1 (*B*).

TABLE 1.—*Effect of solutions of crystalline pepsin upon wool fibers subjected to various treatments*

Previous treatment	Duration of enzyme treatment	30-percent indices	
		Enzyme-treated	Controls
	Days		
None	10	0.96	0.95
Do	30	(1)	.77
Mechanical injury	10	(1)	.96
Reduction	4	(1)	.62
Reduction and reoxidation	10	.94	.94
Reduction and CH_2I	2	(1)	.48
Reduction and CH_2I_2	14	.93	.93

[1] Fibers broke before or during second calibration. See text.

The effect of reduction, or of reduction followed by methylation, was to render the fibers extremely susceptible to digestion by crystalline pepsin. Fibers that had been subjected to either of these chemical treatments and then to the action of pepsin seemed, while still immersed in the enzyme solution, not to have changed greatly in appearance, but were so fragile that attempts to remove them caused them to break into small pieces. A comparison of figure 2 (*A*) with figure 2 (*B*) shows the marked changes produced by the enzyme, including digestion of cortical material, liberation of some cortical cells, and formation of empty tubes of scales. The photographs of cross sections, figure 3 (*A*, *B*, and *C*), demonstrate progressive digestion by pepsin of the cortex of reduced and methylated wool fibers.

Fibers that had been reduced and reoxidized were as stable as untreated fibers toward solutions of crystalline pepsin. Fibers into which new cross-linkages had been introduced by reduction followed by treatment with methylene iodide (according to eq 3) were likewise not attacked.

2. CRYSTALLINE CHYMOTRYPSIN

Pepsin is most active in acid solution, but acid solutions slowly attack the wool and increase its susceptibility to the action of the enzyme. To avoid this complication, it appeared desirable to study the effect upon wool of an enzyme active at a neutral pH value. Crystalline chymotrypsin, which occurs in pancreatic juice along with crystalline trypsin and other enzymes, is active at pH 7.0. Although this enzyme was found to attack reduced and reduced and methylated wool somewhat less rapidly than does pepsin, its action resembled that of pepsin in that it digested the cortex but not the cuticle. Furthermore, untreated wool fibers and those that had been reduced and alkylated with methylene iodide were not attacked (table 2).

TABLE 2.— *Effect of solutions of crystalline chymotrypsin upon wool fibers subjected to various treatments*

Previous treatment	Duration of enzyme treatment	30-percent indices	
		Enzyme-treated	Controls
	Days		
None	7	0.99	0.99
Mechanical injury	7	(1)	.95
Reduction	4	(1)	.55
Reduction and reoxidation	7	.97	.99
Reduction and CH_3I	4	(1)	.41
Reduction and CH_3I_3	7	.89	.91

[1] Fibers broke before or during second calibration.

3. CRYSTALLINE PAPAIN

Neither untreated wool, nor any derivative of wool studied, was attacked by solutions of crystalline papain. In all cases, the 30-percent indices of the enzyme-treated fibers were very close to those of the "control" fibers. The derivatives included wool that had been reduced, reduced and reoxidized, reduced and methylated, and reduced and treated with methylene iodide (table 3).

TABLE 3.— *Effect of solutions of crystalline papain upon wool fibers subjected to various treatments*

Previous treatment	Duration of enzyme treatment	30-percent indices	
		Enzyme-treated	Controls
	Days		
None	7	0.99	0.99
Reduction	7	.55	.55
Reduction and reoxidation	7	.94	.94
Reduction and CH_3I	7	.43	.43
Reduction and CH_3I_3	7	.83	.89

4. CRYSTALLINE TRYPSIN

Untreated wool fibers were not attacked by trypsin, even after prolonged exposure of the fibers to sterile solutions of this enzyme. Similarly all of the treated fibers, except those that had been reduced

alone, were unaffected. Reduced fibers, however, appeared to be slightly attacked, since many of them broke at 20- to 25-percent elongation (table 4).

Although the optimum pH value for the action of trypsin is nearer 8 than 7, the trypsin solutions were adjusted to the latter pH value in most of the experiments in order to avoid extraneous effects due to alkali. Further experiments have now shown that solutions of crystalline trypsin do not digest untreated or reduced and methylated wool even at pH 8.0.

TABLE 4.—*Effect of solutions of crystalline trypsin upon wool fibers subjected to various treatments*

Previous treatment	Duration of enzyme treatment	30-percent indices	
		Enzyme-treated	Controls
	Days		
None	14	0.98	0.98
Mechanical injury	10	.95	.96
Reduction	7	(1)	.60
Reduction and methylation	7	.48	.55

[1] Fibers broke after 20- to 25-percent extension.

5. COMMERCIAL TRYPSIN

Commercial trypsin is a relatively crude preparation made from pancreatic juice and consists of a mixture containing proteolytic enzymes active at a pH value of 7.0. Since it has been used extensively by earlier investigators, it appeared advisable to conduct a few experiments with it in the present investigation. The effects of commercial trypsin upon the fibers are much like those of crystalline chymotrypsin. Fibers that were untreated, reduced and reoxidized, or reduced and treated with methylene iodide were not affected by the enzyme. Reduced and methylated fibers were readily attacked (table 5). Commercial trypsin acted more slowly, however, and never produced as complete digestion of the cortex of the fibers as did crystalline pepsin. Since commercial trypsin attacks wool and crystalline trypsin does not do so, it is evident that some constituent other than crystalline trypsin, possibly crystalline chymotrypsin, is responsible for the action of the commercial product upon the fiber.

TABLE 5.—*Effect of solutions of commercial trypsin upon wool fibers subjected to various treatments*

Previous treatment	Duration of enzyme treatment	30-percent indices	
		Enzyme-treated	Controls
	Days		
None	7	0.99	0.99
Mechanical injury	7	(1)	.96
Reduction and reoxidation	7	.89	.89
Reduction and CH_2I	2	(1)	.47
Reduction and CH_2I_2	7	.91	.91

[1] Fibers broke before or during second calibration.

IV. DISCUSSION

The experiments described in the preceding sections show that wool fibers, when chemically unchanged and mechanically intact, are not attacked by sterile solutions of any of the enzymes studied. The present methods permit more exact interpretations and reveal some of the reasons why earlier experiments have sometimes indicated that wool is digestible by enzymes. Since detailed information has generally not been given in earlier published accounts, no attempt is made to consider each report individually. Results based upon wool that has previously been treated with alkali [4, 5, 15, 16] or with other chemical agents which do not react solely with disulfide groups [4, 6, 9, 10], or that has received mechanical treatment [11], do not provide clear evidence regarding its stability to enzymes. Particularly noticeable in the literature is the absence of statements regarding the sterility of the enzyme solutions. That this is important is shown by the fact that wool kept in a solution of commercial trypsin to which a small crystal of thymol has been added is not noticeably attacked after several weeks, and that wool in a similar, but thymol-free solution shows rapid digestion and evolution of hydrogen sulfide. The effect is apparently a result of the action of microorganisms which attack disulfide groups as well as hydrolyze peptide linkages.

Modified wool fibers may be attacked by enzymes in at least two different ways, depending upon whether the fibers have been modified by mechanical or by chemical means. Mechanically injured wool was attacked by pepsin, but was only broken down into spindle-shaped cortical cells. Even after several months over 90 percent of the wool could be recovered in the form of these cells. However, chemical modification that involves rupture of the disulfide cross-linkages of the wool renders the cortex of the fibers completely digestible. For example, reduced and methylated wool (cystine content, 2 percent) was almost completely digested by pepsin after 2 weeks. The residue, which consisted principally of scale substance, amounted to only 5 percent of the weight of the wool. Since the effects of the two modes of attack are very different, they are discussed separately in the following sections:

1. DIGESTION OF MECHANICALLY INJURED WOOL FIBERS

Pepsin and chymotrypsin attack mechanically injured fibers, but in a way best discussed after considering the histology of the fibers. Wool fibers are not homogeneous but consist of cellular units, arranged in three layers: an outer cuticle consisting of scale cells; a middle region called the cortex, made up of spindle-shaped cortical cells; and a central core or medulla. In many types of wool, the medulla may be very small or absent. After mechanical injury the fibers are attacked and cortical and scale cells are liberated, but these do not appear to be digested by the enzymes. An attack of this type apparently does not result in the digestion of the principal fibrous protein of the wool; rather the appearance of the product suggests that an intercellular substance may have been digested. Such an explanation has already been offered for the action of commercial trypsin on wool by Stakheeva-Kaverzneva and Gavrilov [15], and by Speakman and McMahon [16].

Apparently the impermeability of the cuticle is an important factor in the resistance of chemically unchanged fibers to digestion by enzymes. Mechanical injury of the cuticle or, as will be discussed later, rupture of the disulfide cross-linkages, increases its permeability and facilitates attack. Further evidence of this impermeability is shown by the fact that the cut ends of fibers (either chemically unchanged or reduced and methylated) are more readily attacked than other parts [17].[6] The permeability of the cuticle undoubtedly varies considerably with different types of wool, since these are attacked by enzymes and also absorb dye at very different rates under identical conditions. Damage to the cuticle during chemical or mechanical processing of commercial wools probably contributes to the conflicting results reported in the literature concerning the attack of wool by enzymes.

2. DIGESTION OF CHEMICALLY MODIFIED WOOL FIBERS

The digestion of cortical material was almost complete after the disulfide cross-linkages had been broken by reduction, or by reduction followed by methylation. When the cross-linkages were rebuilt, either by reoxidation of the sulfhydryl groups to disulfide groups, or by their conversion to *bis*-thioether groups ($-S-CH_2-S-$), the resistance to digestion of the original wool was restored.[7] Thus, the resistance appears to be due, not to the chemical nature of the groups involved, but to the existence within wool of a compact three-dimensional polymeric structure, which is a result of the presence of disulfide cross-linkages between polypeptide chains.

A more detailed consideration of the chemistry of polymerization supports this hypothesis. Reduced wool probably consists of polypeptide chains containing cysteine residues. In the sense of Carothers' [19] definition, these polypeptides are linear polymers bearing functional groups capable of reacting with each other to yield a three-dimensional polymer. That is, oxidation of the reduced wool would form disulfide cross-linkages between different polypeptide chains and yield polymers of high molecular weight.

The formation of polymers of high molecular weight from molecules that bear more than one functional group is favored when the concentration of a reactant is high. At lower concentration, lower degrees of polymerization and even reactions to form monomers are to be expected [20]. This means that the formation of disulfide cross-linkages between different polypeptide chains should be favored in reduced wool *fibers*, because the concentration of the reactant (reduced protein) is extremely high. The reoxidation of wool by the method of Goddard and Michaelis, in which reduced wool is *dissolved* in alkali and then treated with an oxidizing agent, should result in a lower degree of polymerization and should favor the formation of disulfide links between different parts of single folded chains. That the amorphous products obtained by these authors may be of this nature is suggested by their high solubility in dilute solutions of acids or alkalies, in which reoxidized wool fibers of the type obtained in the present study are almost completely insoluble.

[6] The penetration of large dye molecules into wool fibers seems to be analogous, since, as has been shown by Millson, Royer, and Wissemann [18], the rate of penetration is increased in injured fibers. Likewise, the rate of penetration of dye into wool in which disulfide cross-linkages have been ruptured is also increased.

[7] Wools of this type have now been shown to be even more resistant to enzymes, bacteria, fungi, and moths than the original wool [22].

The resistance of the cortex of wool to digestion by enzymes, then, appears to be due to its compact three-dimensional polymeric structure. A structure of this sort might resist attack by enzymes through two mechanisms: (1) by keeping the molecules of enzyme from penetrating the structure, (2) by interfering with free rotation of the units of the peptide chains into the special configurations believed to be favorable for enzyme action [21].

Goddard and Michaelis have suggested that a definite physical pattern imparts to wool protein its resistance toward enzymes. The present work indicates that all that may be required is the formation of polymers of extremely high molecular weight and compact structure.

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THE PLANOFLEX, A SIMPLE DEVICE FOR EVALUATING THE PLIABILITY OF FABRICS

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ABSTRACT

The Planoflex, a simple device for measuring the extent to which a fabric can be distorted in its own plane without producing wrinkles on its surface, was developed to evaluate the pliability of woven fabrics. Results of measurements on a series of cotton percales show an 88-percent correlation with their tactual pliability ratings. Comparison of the Planoflex with the Schiefer Flexometer and the Peirce Hanging-Heart Loop methods for evaluating pliability showed it to be as good as or better than these instruments with respect to the extent of the correlation between measured values and tactual pliability ratings, sensitivity to small differences in pliability, and ease of operation. The Planoflex may be used for testing all woven fabrics except those that are heavily starched.

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I. INTRODUCTION

During a study of the evaluation of the "hand" or "feel" of fabrics by objective means, particularly with respect to the pliability of fabrics or the ease with which they could be bent in the hands, it was observed that fabrics differed in the extent to which they could be distorted in their own planes without producing wrinkles on their surfaces. Furthermore, it was observed that the extent of this distortion for similarly constructed fabrics indicated their ease of bending. The desirability of having a method for evaluating pliability more practical and sensitive than those at present available led to further investigation of this distortion characteristic and resulted in the development of the Planoflex, which is described in this paper.

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Pliability is one of the components of hand usually judged by handling a fabric, and it depends chiefly on the ease of bending, or flexibility, of a fabric.[2] It depends also on a fabric's thickness and weight and, less directly, on its compressibility and surface friction. Since measurements of the ease of bending of fabrics by different testing methods involve these other characteristics to varying extents, the criterion of a suitable testing method, aside from its practicability and sensitivity, is the extent to which its results indicate pliability as appreciated by the hands.

Methods for evaluating pliability have been described by Peirce [1],[3] Schwarz [2, 3], Clark [4, 5], Schiefer [6], Gurley [7], and Saxl [8]. They measure either the deflection of a specimen produced by the weight of the specimen itself or the force required to produce a given deflection. The results are affected to a greater or lesser extent by the weight and thickness of the specimen. Some of the methods are not satisfactory for lightweight, soft-finished fabrics and others are considered too insensitive or too difficult to use for many purposes. The Peirce Hanging-Heart Loop method [1] and the Schiefer Flexometer method [6], representative of these two types of methods, were compared with the Planoflex method in the present work.

II. DESCRIPTION AND USE OF THE PLANOFLEX

The Planoflex is shown in figure 1. It consists of a metal base plate supported by a wooden frame, to which is fastened a movable clamp, *A*, a fixed clamp, *B*, and a hinged shelf. Clamp *A* is constrained by two connecting strips to move in an arc of 6-in. radius in such a way that it remains parallel to clamp *B*. A weight clamp, supported by the hinged shelf, is used to put the test specimen under a 2-lb tension when it is mounted.

A specimen 3 in. wide and 10 in. long, cut with the long dimension either parallel or perpendicular to the warp yarns of the fabric, is used for the test. A template may be used for cutting the specimen to size. It is essential that at least one edge of the specimen be parallel to the yarns in the lengthwise direction, a condition that is most easily obtained by gently pulling off a few yarns on one or both edges of the test specimen. A variation of $\pm \frac{1}{16}$ in. in the width of the specimen will not produce any appreciable variation in the result.

A specimen is mounted in the Planoflex as follows. One end is fastened centrally in the weight clamp, care being taken to have the crosswise yarns parallel to the edge of the clamp. Clamp *A* is moved into the position that makes the lengthwise edge of the specimen intersect corresponding points on the edges of the two clamps, *A* and *B*. Scales before the edges of these clamps assist in bringing clamp *A* into proper alinement. The test specimen is then fastened securely in clamp *A*. The hinged shelf is released and held in a vertical position by a spring clip so that the weight clamp hangs freely from the end of the specimen, subjecting it to a 2-lb tension. Then clamp *B*

[2] The terminology used in this paper is that proposed jointly by the American Society for Testing Materials and the American Association of Textile Chemists and Colorists [see Am. Dyestuff Reptr. **29**, 560 (1940)]. The term "flexibility" is used to designate the physical property of a fabric that has to do with its ease of bending. Although it is not quantitatively defined, it would be measured by some objective means. The terms "pliable" and "stiff" and their derivatives describe the ease of bending when determined by the hands, and thus involve sensitivity of touch and the ability of the nervous system to discriminate between different physical properties of the fabric.

[3] Figures in brackets indicate the literature references at the end of this paper.

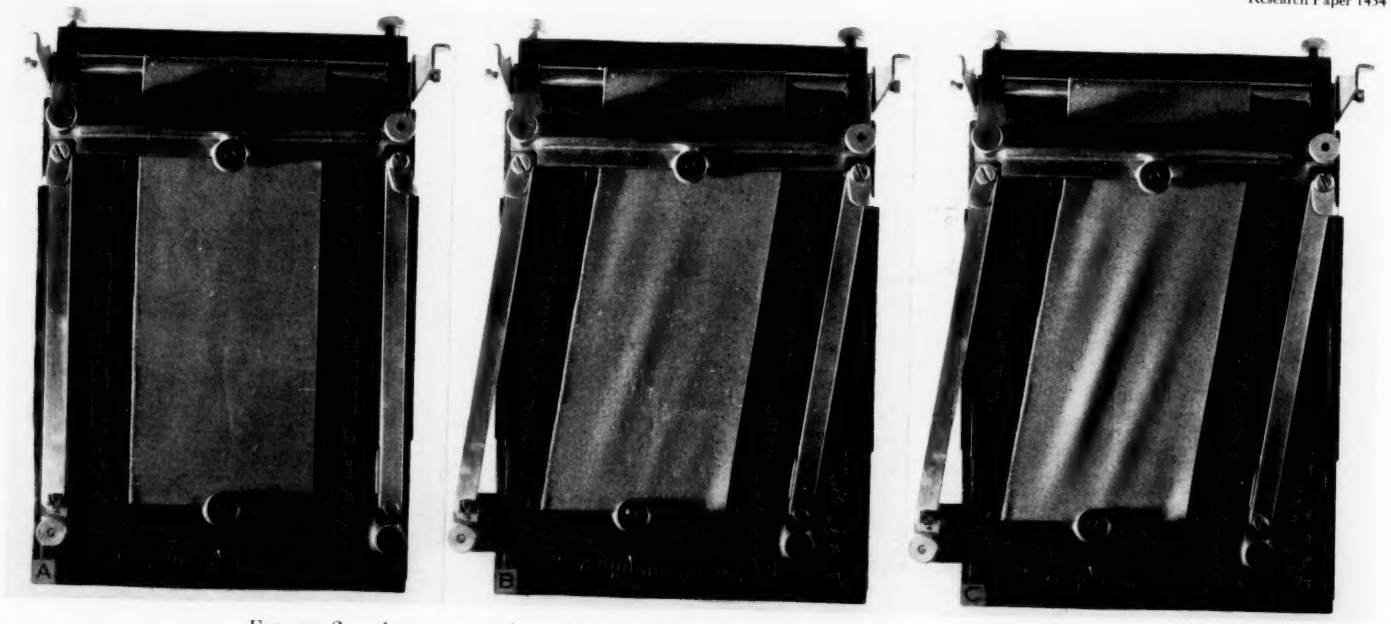

FIGURE 2.—*Appearance of specimen in Planoflex at three stages during the measurement.*

A, Specimen before deflection; *B*, wrinkles at end point; *C*, wrinkles 1 degree beyond end point.

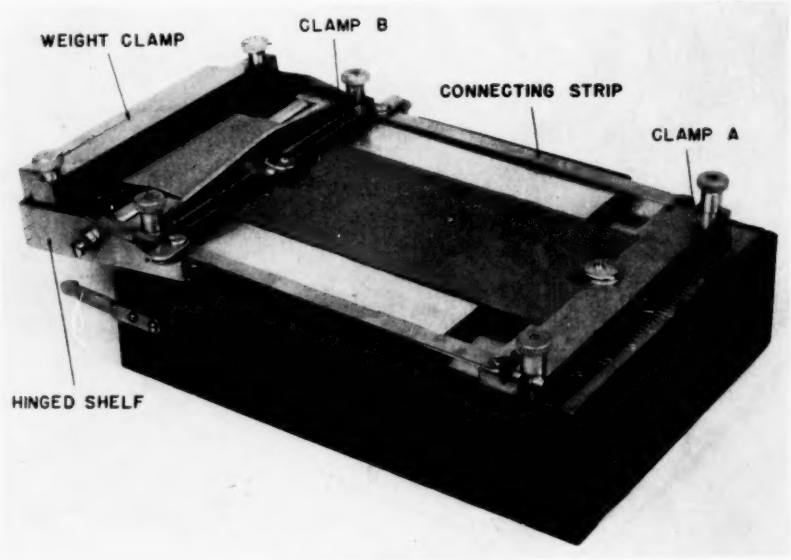

FIGURE 1.—*Planoflex.*

is tightened and the specimen is ready for test. The thumb nuts on clamps *A* and *B* are on toggle bolts, which may be swung out of the way, thus permitting easy removal and replacement of the clamp jaws.

To make the measurement, clamp *A* is moved slowly, first to the left and then to the right, to the angles at which longitudinal wrinkles first appear on the surface of the specimen. These angles, in degrees, are read on the scale below the pointer on clamp *A*. Greater precision is obtained by repeating this operation two or three times before recording the points at which longitudinal wrinkles first appear. The total angle through which the fabric can be distorted in this manner is the sum of the readings obtained on the left and on the right of the center.

The appearance of wrinkles is more readily observed if a lamp is placed about 1 ft to either side of the instrument and 6 in. above its surface. Figure 2 shows how the specimen appears at three stages during the measurement. Figure 2 (*A*) shows the appearance of a specimen before deflection. Figure 2 (*B*) shows the appearance of the same specimen when wrinkles were just visible on the leftward swing of the movable clamp. Two small wrinkles, one in the upper left-hand corner and the other in the lower right-hand corner of the specimen, appeared shortly after deflection of the specimen. These were ignored. The larger wrinkles running across the entire surface of the specimen determine the end point of the motion. Figure 2 (*C*) shows the appearance of the same specimen deflected 1 degree beyond the proper end point. The marked increase in the size of the wrinkles indicates the precision with which the end point can be determined.

The ease and precision with which wrinkles may be determined visually makes the Planoflex a very simple instrument to use. However, the end points of motion may be determined objectively, if desired, by using a scanning bar, which, when raised by a wrinkle, completes an electric circuit. Such a device was found to be satisfactory, although it has no particular advantage over the visual method of observing wrinkles.

III. RESULTS OF PLANOFLEX MEASUREMENTS AND EXPERTS' RATINGS OF PLIABILITY

Nineteen 80×80 cotton percales were used for the principal investigation. These fabrics were products of 10 different manufacturers and included printed and piece-dyed fabrics. Their warp counts averaged 86.5 threads per inch, their filling counts averaged 74.5 threads per inch and their weights averaged 4.85 square yards per pound. The variations from these average values were very small and are not believed to have affected the results.

The relative order of these fabrics, from the most pliable to the stiffest, was determined independently by each of eight textile men experienced in handling fabrics of this type. The average of the eight individual relative ratings for each fabric was taken to represent each fabric's relative pliability. The "average mean deviation"[4] of the experts' individual ratings for pliability was ±1.6 units of rating. The fabrics are listed in table 1 in the order of decreasing pliability

[4] The "average mean deviation" is used in this paper to signify the average, for all fabrics, of the average deviation from the mean of the observations for each fabric.

(increasing stiffness), as determined by the average of the experts' ratings. They were numbered to correspond with their positions in this table.

TABLE 1.— *Results of tests with Planoflex Flexometer and Hanging-Heart Loop on percales*

Fabric number	Experts' average pliability rating	Dreby Planoflex angle	Schiefer Flexometer torque	Peirce Hanging-Heart Loop bending length
		Degrees	*g-cm*	*cm*
1	1.9	12.3	101	1.54
2	3.9	12.0	111	1.74
3	4.1	11.3	122	1.80
4	4.5	10.8	120	1.57
5	4.5	10.5	122	1.63
6	5.4	8.5	123	1.49
7	6.6	10.3	117	1.55
8	8.4	16.8	109	1.62
9	8.9	8.5	122	1.76
10	10.4	7.5	143	1.76
11	11.2	6.5	147	1.66
12	11.4	7.0	168	1.82
13	12.4	11.5	122	1.58
14	14.5	4.3	166	1.67
15	15.2	3.0	184	2.07
16	15.5	6.5	194	1.73
17	15.5	3.8	207	1.83
18	17.6	1.8	230	1.82
19	18.3	4.0	214	2.13
Average mean deviation	±1.6	±0.4	±7	±0.04

The results of the measurements of the percales with the Planoflex are also given in table 1. Preliminary studies with these fabrics showed that the measurement of two specimens was adequate to obtain a reproducible average value of the angle and that it was only necessary to measure specimens cut in one direction, since the angles for specimens cut in the fillingwise and warpwise directions differed by less than 0.5 degree. Accordingly each reported value is the average of the angles observed for two specimens, both cut with the long dimension in the direction of the warp yarns, since it is easier to cut fabric specimens straight in this direction. The average deviation of the observed angles from their mean varied, depending on the magnitude of the observed angle (±0.8 degree when the observed angle was 16.8 degrees to ±0.3 degree when the observed angle was 1.8 degrees). The average mean deviation of the Planoflex results for all fabric specimens was ±0.4 degree. All the measurements were made on samples conditioned at least 24 hours in air having a relative humidity of approximately 65 percent and a temperature of approximately 70° F.

In order to determine the extent to which the results of measurements with the Planoflex correlate with the tactual ratings of pliability, the fabrics were first listed by sample number in the order determined by each of the two methods of ranking, as follows:

Planoflex	8	1	2	13	3	4	5	7	6	9	10	12	11	16	14	19	17	15	18
Experts	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19

According to the Planoflex method, fabric 8 was first, with the largest angle (16.8 degrees), and fabric 18 was last, with the smallest angle

(1.8 degrees). According to the tactual method, fabric 1 was first, with the lowest average pliability rating (1.9 units), and fabric 19 was last, with the highest average pliability rating (18.3 units). The objective order of the fabrics in each series was then correlated by the procedure described by Kendall.[5]

The correlation coefficient obtained was 72 percent. As shown by the arrangement of the fabrics above, fabrics 8 and 13 are the only ones markedly different in the two series. Without these two samples the correlation is 88 percent, indicating very good agreement between these two methods. These correlation coefficients were computed without regard to the differences between the measured values of the fabrics in each of the two series, many of which were less than the error of measurement. If consideration were given to these small differences in determining the objective order of the fabrics, it would be possible to show an even higher correlation between the Planoflex and tactual methods of evaluating pliability.

The anomalous behavior of fabrics 8 and 13 was also noted in the results of tests with the Flexometer and Hanging-Heart Loop methods, which will be given later. The agreement in results among the three test methods on the one hand and among the eight experts on the other as to the relative positions of these two fabrics in the series indicates that some characteristic or condition of these fabrics, not present in the others, has entered into the determination of their pliabilities. The differences between the number of yarns per inch, weight, thickness, coefficient of friction, resilience, and compressibility of these fabrics and the respective properties of the other fabrics have been examined, but they do not offer any explanation of the lack of agreement between measured and tactual ratings of these fabrics.

To compare the relative sensitivities of the Planoflex and the hands to the differences in pliability of these fabrics, the ratio of the spread of values obtained to their average mean deviation was determined for each series of values. This ratio is an indication of the number of distinct regions within the range of pliability exhibited by these fabrics which might be detected by the method of measurement. The data for the Planoflex gave a ratio of 37, whereas the tactual data gave a ratio of only 10. The sensitivity of the Planoflex relative to the hands may not be as great as indicated here, but it is apparent that it is considerably more sensitive.

IV. COMPARISON OF THE PLANOFLEX AND OTHER METHODS FOR EVALUATING PLIABILITY

To compare the Planoflex with other testing devices for evaluating pliability, the series of nineteen 80×80 cotton percales were measured with the Schiefer Flexometer and the Peirce Hanging-Heart Loop.

The Schiefer Flexometer is an instrument for measuring the torque exerted by a pair of specimens, so mounted as to balance out their weight, when folded to some predetermined angle. Preliminary

[5] The Kendall coefficient of correlation between two series of rankings is given by the equation $2\Sigma/n(n-1)$ where n is the number of members ranked and Σ is computed as follows: The members are put in objective order in the one series, which then determines the corresponding order of the rankings for the other series. Each member in turn of the latter sequence of rankings is compared with succeeding members in the sequence. Those pairs in the correct sequence are given a value of +1 and those in the inverted sequence are given a value of −1. The sum of these values is denoted as Σ. The method is described in detail by Schwarz and Winn [Technical Evaluation of Textile Finishing Treatments. III. Use of Rank Correlation for Comparison of Data. Am. Dyestuff Reptr. **29**, P400 (1940); Textile Research **10**, 453 (1940).]

studies showed that the geometric mean of the torques for an angle of fold in degrees equal to 430 times the thickness of the fabric in inches for warpwise and fillingwise directions gave the most satisfactory results. Four pairs of specimens of each fabric were measured, two prepared with the long dimension in the direction of the warp yarns and two with the long dimension in the direction of the filling yarns. The geometric means of the average values for warpwise and fillingwise directions are reported in table 1. The average mean deviation of the Flexometer results for all fabric specimens was ± 7 gram-centimeters.

With the Peirce Hanging-Heart Loop method, the extension of a strip of fabric in the form of a heart-shaped loop is measured, the extension being produced by the weight of the fabric itself. Four specimens of each fabric were measured, two prepared with the long dimension in the direction of the warp yarns and two with the long dimension in the direction of the filling yarns. The geometric means of the average values for warpwise and fillingwise directions are reported in table 1. The average mean deviation of the Hanging-Heart Loop results for all fabric specimens was ± 0.04 centimeter.

The correlation between the order of the fabrics determined by these two methods and the order determined by the tactual pliability ratings was determined by the Kendall method described before. For all 19 fabrics the Flexometer showed a correlation of 79 percent and the Hanging-Heart Loop, 49 percent. Fabrics 8 and 13 were displaced in the same direction relative to the other fabrics by the Flexometer results as they were by the Planoflex results, and they also accounted for most of the disagreement between the Flexometer ranking and the experts' ranking of the percales. Of the same two fabrics, only fabric 13 showed marked disagreement between the Hanging-Heart Loop ranking and the experts' ranking of the percales. When both these fabrics were removed from the series, the correlation coefficient was 88 percent for the Flexometer and 51 percent for the Hanging-Heart Loop. Thus the Planoflex and Flexometer methods are about comparable with respect to the correlation of their results with tactual pliability ratings and somewhat better than the Hanging-Heart Loop method.

To compare the sensitivities of these methods with the Planoflex and the hands, the ratio of the spread of values obtained to their average mean deviation was determined for each series of values as described before. The Flexometer data gave a ratio of 18 and the Hanging-Heart Loop data a ratio of 16, compared with 37 for the Planoflex and 10 for the hands. Each of the three testing methods is more sensitive than the hands, and the Planoflex is most sensitive.

In addition to the differences between the Planoflex, Flexometer, and Hanging-Heart Loop methods with respect to the correlation of their results with pliability and their sensitivity, there are several differences with respect to their ease and convenience of operation that are of considerable importance in applying them to routine testing. The Planoflex, insofar as it has been tested on different types of fabrics, is the only method that gives results which are for all practical purposes independent of the warpwise or fillingwise direction. All of the area of the specimen is distorted during the test, as compared with the relatively small part of the fabric specimen bent in the other tests. These conditions permit the measurement of fewer specimens to

obtain a reproducible average value. The operation of cutting out and setting up a test specimen is done very easily. The instrument is direct reading. A complete test, including the preparation and measurement of three specimens of a fabric, can be completed in less than 5 minutes, excluding the time for conditioning the specimens. The mounting of the specimens for the Flexometer and their insertion in the instrument are delicate and tedious operations. The measurement itself is easily made, but there are subsequent corrections for zero points and spring calibrations that have to be made to obtain the value that is used as the measure of pliability. The Hanging-Heart Loop method utilizes the simplest apparatus. A definite technique in handling specimens for this test has to be developed to avoid erratic results. The observed values must be converted by means of the formula derived by Peirce to the quantities that indicate pliability.

V. DISCUSSION OF THE BEHAVIOR OF FABRICS IN THE PLANOFLEX TEST

A consideration of the conditions involved in the Planoflex test will make more apparent the uses and limitations of the Planoflex for evaluating pliability.

The contribution of the physical properties of a specimen to its angle of distortion seems to be of two kinds.

First, there is a certain amount of free space between the yarns of the specimen that permits relative rotation of the warp yarns and the filling yarns at their intersections throughout the specimen. The free space available depends mainly on the size of the yarns and the number of yarns per inch. Since the contribution of this freedom of motion to the total angle of distortion is relatively large and practically independent of all but dimensional characteristics of the yarns, it cannot be expected that results with the Planoflex on differently constructed fabrics will be comparable.

After the free space is taken up, however, the yarns themselves are subjected to compression, as continued distortion of the specimen reduces its area. Depending on the physical characteristics of the yarns, a condition of instability is reached that results in a sudden disruption of the surface of the specimen. The ability of the yarns to give during this stage of the distortion is apparently intimately related to their flexural characteristics, since on similarly constructed fabrics the results of measurements with the Planoflex, Flexometer, and Hanging-Heart Loop are in substantial agreement. Other physical properties of the yarns, notably their surface friction and density, undoubtedly affect the extent of the distortion of the specimen. It would appear that either their effects are too small in proportion to the effects of the flexural properties or their effects complement the effect of the flexural properties in giving values that indicate pliability.

Since it is necessary to put the specimen under tension in order to obtain reproducible results, the specimen of any fabric that is too readily stretched will, after mounting, have a different construction insofar as the test is concerned than the fabric which it is supposed to represent. Thus measurements on fabrics which may have identical

construction but which have different extensibilities will not be on a comparable basis.

VI. USES AND LIMITATIONS OF THE PLANOFLEX TEST

The Planoflex is well adapted to testing a wide variety of fabrics, as shown by measurements on the following representative types: cotton print cloths, broadcloths, poplins, organdies, twills, and sateens; rayon French crepes, twills, satins, and spun rayon fabrics of challis-like and linen-like finish; and wool and mixed wool-rayon uniform suitings and shirtings. With the exception of a very few fabrics in some of the groups, the results of measurements with the Planoflex were in agreement with the pliability ratings of these fabrics determined tactually by experts. The order of magnitude of the values obtained for the particular fabrics representing these several types is indicated in table 2.

TABLE 2.—*Range of Planoflex values for different types of fabrics*

Fabric	Range
	Degrees
Cottons:	
80×80 print cloths	2 to 16.
68×72 print cloths	10 to 25.
100×60 broadcloths	8 to 15.
100×40 poplins	12 to 23.
76×72 organdies	36 to 54.
68×76 twills	5 to 10.
65×110 sateens	2 to 30.
Rayons:	
165×72 crepes	29 to 35.
116×67 twills	36 to 42.
225×65 satins	37 to 44.
68×62 spun rayons:	
Challis-like	36 to 43.
Linen-like	31 to 35.
Wool and mixed wool-rayon:	
Uniform suitings	11 to 17.
Uniform shirtings	20 to 28.

Like other instruments for evaluating pliability, the Planoflex cannot be used indiscriminately to evaluate the relative pliabilites of fabrics of different construction. By different construction is meant different fiber construction, different yarns per inch in either direction, and different weight. Variations of ± 5 percent in either the count or the weight of a group of fabrics should be considered the limits within which the results with the Planoflex are on a comparable basis. With fabrics having greater variations in these properties than the above, the results with the Planoflex should be examined carefully before any significance is attached to them. A few special fabrics, like tracing cloth, in which a heavy coating of starch has cemented warp and filling threads together, will not give measurable results on the Planoflex. Knit fabrics are too easily distorted and stretched to give values of any significance.

In addition to the use of the Planoflex for quantitatively evaluating pliability, there are two other uses to which the instrument can be applied with distinct advantage—namely, the evaluation of the effect of different finishing agents and technical control during finishing operations.

With a sensitive, reliable instrument for indicating quantitatively the effect of different finishing agents on a fabric, a finisher can select with greater certainty the better finishing agents for his purposes, not only with respect to the desirability of their effects but also with respect to the economy of their use. It should be pointed out that finishing agents have greater effects on some fabrics than on others, depending on the nature of the construction of the fabric and the magnitude of its effect on the hand in relation to the magnitude of the effect on the hand induced by the finishing agent. In addition, the relative effects of different finishing agents quite frequently vary when applied to fabrics made of different kinds of fibers. These facts make it clear that the selection of a finishing agent should be based upon the results of measurements on the same type and construction of fabric to which the agents are to be eventually applied.

The processing of fabrics involves a series of operations, each one of which may have an effect on the hand of the finished fabric. An easily made study of the effect of the different operations on the pliability of a fabric would lead to more accurate control of the operations, resulting in the production or reproduction of more uniformly finished fabrics. For this purpose an instrument, such as the Planoflex, that gives dependable results with a minimum of effort in a very short period of time would be desirable.

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WASHINGTON, September 26, 1941.

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